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Health Impacts, Emissions, and Emission Factors for Noncriteria Pollutants Subject to 'De Minimis' Guidelines and Emitted from Stationary Conventional Combustion Processes

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16. ABSTRACT

Report presents a literature survey of the health and ecological effects associated with various air quality levels of noncriteria pollutants that are regulated under the Clean Air Act. These noncriteria pollutants include mercury, beryllium, asbestos, sulfuric acid mist, vinyl chloride, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, carbon disulfide and carbony sulfide. Nationwide emissions are estimated for each noncriteria pollutant with particular emphasis on contributions from fossil fuel combustion at stationary sources. Factors for quantifying emissions from fossil fuel combustion processes are discussed for each noncriteria pollutant.

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by

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TABLE OF CONTENTS

Page

1. INTRODUCTION AND SUMMARY 1

2. HEALTH AND ECOLOGICAL EFFECTS 5

  2.1 HEALTH AND ECOLOGICAL EFFECTS ON POPULATIONS 6

    2.1.1 Mercury 6
    2.1.2 Beryllium 11
    2.1.3 Asbestos 14
    2.1.4 Fluorides 16
    2.1.5 Sulfuric Acid Mist 20
    2.1.6 Vinyl Chloride 24
    2.1.7 Hydrogen Sulfide 26
    2.1.8 Methyl Mercaptan 29
    2.1.9 Dimethyl Sulfide 30
    2.1.10 Dimethyl Disulfide 31
    2.1.11 Carbon Disulfide 31
    2.1.12 Carbonyl Sulfide 34

  2.2 ECOSYSTEM EFFECTS 35

3. NATIONAL EMISSIONS 37

  3.1 TRACE ELEMENTS 37

  3.2 ASBESTOS 37

  3.3 SULFURIC ACID MIST 41

  3.4 VINYL CHLORIDE 41

  3.5 TOTAL REDUCED SULFUR AND REDUCED SULFUR COMPOUNDS 41

  3.6 SUMMARY OF EMISSIONS 45

4. EMISSION FACTORS 48

  4.1 TRACE ELEMENTS 48

  4.2 SULFURIC ACID MIST 55

  4.3 ASBESTOS AND VINYL CHLORIDE 57

TABLE OF CONTENTS (continued)

Page

5. DEVELOPMENT OF EMISSION FACTORS 58

5.1 TRACE ELEMENT EMISSIONS 58

5.1.1 External Combustion - Utility Boilers 58
5.1.2 External Combustion - Industrial Boilers 62
5.1.3 Internal Combustion - Industrial or Electricity Generation 63
5.1.4 External Combustion - Commercial/Institutional 64

5.2 ASBESTOS EMISSIONS 65

5.3 SULFURIC ACID MIST EMISSIONS 71

5.4 VINYL CHLORIDE EMISSIONS 69

5.5 TOTAL REDUCED SULFUR AND REDUCED SULFUR COMPOUND EMISSIONS 70

6. SAMPLING AND ANALYSIS PROCEDURES USED TO OBTAIN EMISSIONS DATA 72

6.1 SAMPLING METHODOLOGY 72

6.2 ANALYTICAL METHODOLOGY 74

6.3 ADEQUACY OF DATA FOR EMISSION FACTOR DEVELOPMENT 75

6.4 IMPLICATIONS OF EMISSION FACTOR VARIABILITIES FOR EMISSIONS CALCULATIONS 81

APPENDIX A: PERSONS CONTACTED FOR INFORMATION ON TOTAL REDUCED SULFUR AND REDUCED SULFUR EMISSIONS 79

REFERENCES 80

1. INTRODUCTION AND SUMMARY

Rules have been proposed in the September 5, 1979, Federal Register (Volume 44, Number 173) involving the Prevention of Significant Air Quality Deterioration (PSD). If adopted, these would substantially modify the existing procedures for approving the construction or modification of sources of pollutants regulated by the Clean Air Act. A concept discussed in these rules involves the authority of EPA to exempt some situations from PSD review. These situations are called de minimis. Emission cutoffs for twenty pollutants have been published in the Supplementary Information for these rules (44 FR 51937) and are proposed as guidelines to determine if potential emissions from a source subject to PSD review could be considered insignificant. These emissions levels were based on ambient air quality levels considered protective of public health and welfare, and were derived from these air quality levels (44 FR 51938) by means of a conservative modeling analysis. The guideline emission rates and air quality levels for the noncriteria pollutants in this list are shown in Table 1-1.

TRW Inc., Radian Corporation, and Battelle Columbus Laboratories are in the process of developing an extensive information base on environmental health effects, emissions, and pollution control technology for Stationary Conventional Combustion Processes (SCCP) as part of the Conventional Combustion Environmental Assessment (CCEA) program for EPA's Industrial Environmental Research Laboratory. The source categories included as SCCP are shown in Table 1-2.

This report summarizes the results of a quick-response task assignment to TRW and Battelle under the CCEA Systems Contract to use the CCEA information base in developing the following kinds of information for the pollutants listed in Table 1-1:

- Health and ecological impacts associated with de minimis air quality levels.
- Emission factors for SCCP source categories.
- Comparison of emission levels from important source categories for each pollutant.
- Sampling and analysis methods, associated accuracies, and implications of variabilities of emission factors.

TABLE 1-1 NONCRITERIA DE MINIMIS GUIDELINES FOR SIGNIFICANT EMISSION RATES AND AMBIENT AIR QUALITY IMPACTS

Pollutant	Significant Emission Rate (metric tons/year)	Significant Air Quality Impact ($\mu g/m^3$)
Mercury	0.2	0.1 (24 hr)
Beryllium	0.004	0.005 (24 hr)
Asbestos	1	1 (1 hr)
Fluorides	0.02	0.01 (24 hr)
Sulfuric Acid Mist	1	1 (24 hr)
Vinyl Chloride	1	1 (max.value)
Total Reduced Sulfur:		
Hydrogen Sulfide	1	1 (1 hr)
Methyl Mercaptan	1	0.5 (1 hr)
Dimethyl Sulfide	1	0.5 (1 hr)
Dimethyl Disulfide	1	2 (1 hr)
Reduced Sulfur Compounds:		
Hydrogen Sulfide	1	1 (1 hr)
Carbon Disulfide	10	200 (1 hr)
Carbonyl Sulfide	10	200 (1 hr)

Source: Federal Register - September 5, 1979, Pp 51937-8(222.)

This information is developed in this report for all sources shown in Table 1-2. In order to be consistent with the EPA timetable for promulgation of the proposed rules, the following constraints were placed on this assignment:

- Period of performance: two months.
- Resources: only the existing CCEA information base.
- Emission sources considered: stationary conventional combustion processes (SCCP) only.

Normally the Residential sector is included as a fourth emission source category. However, it will not be considered in this study, since residential sources probably will not be subject to PSD regulation. The information listed above and the assumptions and methods used to compile this information are discussed in the following sections.

Although developing conclusions relative to the magnitude of the de minimis emission and ambient levels in the proposed regulation was not one of the objectives of this study, several observations can be made in summary of the information accumulated in this report:

- Health and ecological impacts. The results of the investigation of the health effects of the noncriteria de minimis pollutants vary by pollutant (see Section 2.1). Comparisons of dose-response

TABLE 1-2. MAJOR STATIONARY CONVENTIONAL COMBUSTION PROCESS SOURCE CATEGORIES CONSIDERED IN THIS STUDY

ELECTRICITY GENERATION	INDUSTRIAL	COMMERCIAL/INSTITUTIONAL
External Combustion	External Combustion	External Combustion
Coal Petroleum Gas	Coal Petroleum Gas	Coal Petroleum Gas
Internal Combustion	Internal Combustion	Internal Combustion
Petroleum Gas	Petroleum Gas	Petroleum Gas

information in the literature with the de minimis ambient levels are summarized in Section 2.1. Unfortunately, insufficient information is available in the literature to form substantive conclusions on ecosystem effects (as opposed to health effects) of most of these pollutants (see Section 2.2), and necessary research and synthesis are well beyond the scope of this effort.

- Emission source categories. Stationary Conventional Combustion Processes (SCCP) produce nearly all of the beryllium and sulfuric acid emissions nationally. These sources also account for 65 percent of the fluoride emissions and 25 percent of the mercury emissions. Asbestos, vinyl chloride and all reduced sulfur compounds are emitted exclusively by other (non-SCCP) sources, according to available data. (See Section 3).

- Emission factors. Based on emission factors in the existing information base, emissions of sulfuric acid mist from large coal or oil-fired external combustion systems (utility and large industrial boilers, for example) controlled to meet the New Source Performance Standards (NSPS) will exceed the de minimis emission levels by orders of magnitude. Similarly, fluoride emissions from NSPS-controlled external combustion sources burning coal will exceed the de minimis levels significantly. (See Sections 4. and 5.). Emissions of the remaining noncriteria pollutants from combustion sources will not normally exceed de minimis levels, although the uncertainty of emission levels calculated with the beryllium emission factors is high due to high variabilities of the influence parameters used to develop the factors (see Section 6.).

2. HEALTH AND ECOLOGICAL EFFECTS

Published information on the health and ecological effects of the twelve subject pollutants was identified, assembled, and reviewed. This section summarizes the results of that review. The biological effects information necessary for the completion of this study was obtained in part from a data base assembled at Battelle's Columbus Laboratories for the EPA's Conventional Combustion Environmental Assessment Program. This collection of published material, although small, contains useful data for some of the substances. These data were augmented via the results of computer bibliographic searches. Successful searches on part of the substances were conducted in BIOSIS, AGRICOLA, NTIS, TOXLINE, and TOXBACK for the general period 1970 to 1979. For such topics as odor thresholds, manual searches were carried out using different keywords in order to locate as many germane articles as possible within the scope of work. Much of the human health effects data were obtained from occupational health studies reported by the National Institute for Occupational Safety and Health (NIOSH) in Criteria Document reports for the EPCH chemical.

Although much useful information was obtained from the above sources these should not be considered all inclusive. Additional information sources are available but the level of effort of this task precluded their review. Effort was placed in reporting observed effects from inhalation of low concentrations of the twelve pollutants. Where sufficient data were available they are presented in tables. Dosages reported range from the lowest known to cause a measurable effect to those which generally cause a more deleterious effect. Each table and accompanying text feature several species including plants and animals; however, emphasis is on human responses.

Data reported in tables emphasize biological responses to low levels of the pollutant by various target organisms. The accompanying text discusses the studies most relevant to the de minimis recommendations, thus not all data in the tables are discussed in the text.

Although the availability of low dosage information exceeded our expectations, there remained a general lack of such needed data. Another inherent limitation was the lack of rigorous dose-response curves. Ideally, the dose-response curve would provide a continuous, quantitative relationship of a given response by a given species to a given route of entry; e.g., inhalation. In the absence of such quantitative dose-response curves, numerous dose-response relationships are presented. Here, the emphasis is on the variety of responses by numerous species to various routes of entry (although inhalation was the usual one).

The presentation of the health and ecological effects has been divided into three sections: health and ecological effects, ecosystem effects, and comparison of de minimis levels with the lowest identified exposures known to cause biological effects.

2.1 HEALTH AND ECOLOGICAL EFFECTS ON POPULATIONS

Studies reviewed in this section concentrate on the effects of substances on individual species. Effects observed include odor thresholds, changes in rates of morbidity or sickness, changes in tumor incidence, and other effects associated with humans, plants, and animals. Throughout, the effects on humans are discussed first, followed by effects on nonhumans. Emphasis has been placed on inhalation as the primary route of exposure. However, depending on the substance and species involved, other routes of exposure were considered.

2.1.1 Mercury

The proposed de minimis value for mercury is 0.1 $\mu g/m^3$, 24-hour average. The health effects from mercury vary depending upon the route of exposure and form of mercury encountered.

Exposure to mercury may occur from inhalation of atmospheric mercury, ingestion of mercury contaminated products, and percutaneous absorption of mercury. The research reported below has concentrated on inhalation exposure.

TABLE 2-1. HEALTH/ECOLOGICAL EFFECTS OF POPULATIONS EXPOSED TO MERCURY IN AIR

Exposure Concentration, mg/m^3	Duration of Exposure	Species	Effects	Reference
0.002-0.005	6.5 hr/d,6 d/wk	Rat	Changes in conditioned reflexes	Kournossov 1962 (101), cited in (90.)
0.005-0.06	19 yr	Human	Clinical mercury poisoning - tremors erethism in 1 of 16 exposed workers.	Bistrup, et al, 1951 (84.)
0.01-0.05	>1 yr occupational exposure	Human	'Micromercurialism' – functional changes in cardiovascular, urogenital, endocrine systems. Hyperthyroidism.	Friberg and Vostal, 1972 (90.)
0.01-0.27	variable occupational exposure (1-20+ yrs.)	Human	Anorexia, loss of weight, insomnia, tremors, dose/response relationship shyness, nervousness	Smith, et al., 1970 (103.)
0.01-0.6[a]	9 yr average	Human	Dose/response relationship identified. Tremors, erethism, impaired memory	Turrian, et al., 1956 (104.)
0.01	occupational exposure	Human	Temporary disability, disturbed menstrual function, elevated percentage of complications in pregnancy and delivery.	Goncharuk, 1977 (91.)
0.08[a]	occupational exposure	Human	Borderline symptoms of mercury poisoning.	Neal, et al., 1937, (96.) 1941 (95.)
3.0	continuous	Dog	Gingivitis, diarrhea, weight loss after 15 days	Fraser, et al., 1934 (89.)

[a] Analytic methods suspect. Spot samples obtained, not breathing zone time weighted average (TWA).

However, atmospheric mercury may be incorporated in aquatic and terrestrial environments. Inorganic and organic mercury compounds introduced into these environments may undergo microbial transformation to the more toxic alkyl mercury form. Aquatic organisms biomagnify the alkyl mercury compounds. The partitioning of organic and inorganic mercury compounds within various media and ecosystems is not reported here. A more thorough analysis of this partitioning was not possible in this level of effort.

The health effects data in Table 2-1 are based on respiratory exposures to inorganic mercury compounds in occupational environments. The following narrative reviews some of these data. Bidstrup et al. (84.) reported tremors and erethism in one individual occupationally exposed 9.5 years to inorganic mercury at concentrations of 0.005 to 0.06 mg/m^3 air. However, Friberg and Vostal (90.) question the accuracy of this value as they note only spot samples were used to estimate worker exposure.

Friberg and Vostal (90.) described several Russian studies which reported an asthenic vegetative syndrome diagnosed as micromercurialism. The syndrome was reported in workers exposed to 0.01 to 0.05 mg/m^3 in work room air. The syndrome itself was not clearly defined but included neurasthenic symptoms and was diagnosed by the occurrence of any three of the following symptoms: tremor, thyroid enlargement, increased uptake of radioiodine in the thyroid, hematological changes, hypotension, labile pulse, tachycardia, dermographism and gingivitis.

Smith et al. (103.) identified a dose response relationship in workers occupationally exposed through inhalation of inorganic mercury in the manufacture of chlorine. Anorexia, weight loss, tremors, insomnia, shyness, frequent colds, nervousness, diarrhea, alcohol consumption and dizziness demonstrated a significant positive correlation. The author summarized the clinical results as exhibiting a dose-related response to mercury exposure by evidencing higher incidences of neuropsychiatric symptoms. The authors concluded that, with respect to most of the symptoms, the dose-response relationship does not exhibit sufficiently high incidence to warrant concern unless exposure exceeds 0.1 mg/m^3 air. However, they noted that there did not appear to be a threshold of effect for anorexia and weight loss, but in these instances uncertainties existed which led the authors to express a reasonable doubt as to the significance of the effect.

Skerfving and Vostal (102.) described a hypersensitive reaction in persons orally and dermally exposed to inorganic and organic mercury ointments and teething powders. The disease, known as acrodynia, was characterized by coldness, swelling and irritation of the hands, feet, cheeks and nose, loss of hair, and ulceration. Disease onset was characterized by increasing irritability, photophobia, sleeplessness, and general dehydration. Neurological symptoms were also observed. Mercury exposure was postulated as the etiologic agent, but adequate analysis and elucidation of the mechanisms of the disease was not reported.

Inorganic and organic mercury compounds have demonstrated genetic effects in humans and nonhumans via consumption of fish contaminated with methyl mercury (100.). Ramel (100.) concluded that mercury pollution has reached a level at which genetic effects on human beings do take place, noting that little is known of the medical significance of these chromosomal defects.

The National Research Council (94.) concluded that more subtle effects from mercury exposure, such as behavioral or intellectual deficits, may not be detectable at present due to limitations in clinical procedures of diagnosis. The Council concluded that, in view of the toxicity of mercury and the inability of researchers to specify the threshold levels of toxic effects, on the basis of present knowledge, all such contamination must be regarded as undesirable and potentially hazardous to humans.

For nonhuman receptors, exposure to mercury following microbial transformation and bioaccumulation represents a more serious hazard than inhalation of vaporized mercury. Air borne elemental mercury has an estimated residence time of eleven days, and is removed from the atmosphere by precipitation. It is estimated that 40 percent of the mercury emitted from the stacks of a power generating plant would enter a typical drainage system (99.). Once in the aquatic system, the mercury can be transformed into methyl mercury, a neurotoxin. Jensen and Jernelev (92.) demonstrated that biomethylation of mercury can be accomplished by the microflora in the sediments.

The relative amounts of mono- and dimethyl-mercury compounds produced are a function of temperature, pH, mercury concentration, organic pollution load, and the microbial population. Low concentrations of mercury tend to favor the formation of dimethyl mercury, a relatively inert compound, while higher concentrations of mercury favor the formation of monomethyl mercury. In neutral and alkaline environments, dimethyl mercury transformation is favored. Dimethyl mercury thus produced will decompose to monomethyl mercury in a slightly acid condition (88.).

Potter et al. (99.) studied the bioaccumulation of mercury through the food chain of Lake Powell, Utah and found that, compared to the mercury in the water, mercury in fish in the upper trophic level had increased by a factor of 43,000. Thus, many of the effects of mercury cannot be related to a single direct dosage; an organism can receive additional dosages from eating mercury contaminated prey.

The LD_{50}* values for intertidal red algae sporelings range from 3.0 to 8.0 mg/l in water (86.). Boney (85.) however found a 40 percent inhibition of growth in the red algae Plumaria elegans 21 days after the sporeling was immersed in a 0.12 mg/l mercuric chloride solution for 24 hours.

Terrestrial animals also bioaccumulate mercury. Even though concentrations of atmospheric mercury may be lower than what would directly evoke a biological response, the indirect (food chain) effects can be considerable. For example, even though the half-life of methylmercury in mice is 3.7 days (97.), the white-footed deer mouse (Peromyscus maniculatus) can accumulate enough mercury to impair swimming and open field behavior (87.).

Other studies involving ingestion of mercury by rodents demonstrated that relatively low dosages cause little to no effects. For example, 0.22 ppm of continuous exposure in food for two years caused no ill effects to rats in either reproduction or histopathology (98.). Dosages of one mg/kg/day of continuous feeding caused a depressed rate of body weight gain after 70 days and mild to severe motor disturbance in five of 18 rats after 70 days (93.).

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*Lethal Dose Fifty - a calculated dose of a substance which is expected to cause the death of 50 percent of an entire defined experimental animal population, as determined from the exposure to the substance by a route other than inhalation of a significant number from that population (244.).

Kournossov (101., cited in 90.) observed changes in conditioned reflexes in rats exposed to atmospheric concentrations of mercury vapor at 0.002 mg/m^3 to 0.005 mg/m^3. However, Friberg and Vostal (90.) concluded that the significance of these changes is difficult to evaluate due to inadequate descriptions of study methods.

2.1.2 Beryllium

The proposed *de minimis* level for beryllium is 0.005 μg/m^3, 24-hour average. Several generalities are evident from the literature examined. The toxicity of beryllium is dependent on its form. For example, beryllium fluoride is more toxic than beryllium sulfate or beryllium oxide; in other words, the more water soluble the compound, the more rapid and severe the response. The toxicity of beryllium oxide depends on its chemical and physical properties. When injected intratracheally, high-fired beryllium oxide (calcinated at 1600°C) resulted in fewer adenocarcinomas and minor cellular reaction in rats as compared to the low-fired oxide (calcined at 1100°C and 500°C) (117., cited in 113.).

Respiratory exposure to beryllium in occupational environments was used as the basis for evaluating the human health effects summarized in Table 2-2. Respiratory exposures to beryllium have produced both acute and chronic effects. These effects have been differentiated by time between exposure and onset of disease, and by the duration, type, and severity of health effects. Acute manifestations of beryllium disease have occurred at high concentrations in excess of 100 μg/m^3 (105.). The Beryllium Case Registry has reported one case of chronic beryllium disease after 9.5 years exposure to 2.0 μg/m^3 beryllium daily weighted average (range 0.7 to 5.9 μg/m^3) (113.). Further investigations have indicated that this exposure may have been greatly underestimated (113.). The correlation of exposure

TABLE 2-2. HEALTH/ECOLOGICAL EFFECTS OF POPULATION EXPOSED TO BERYLLIUM IN AIR

Exposure Concentration, ($\mu g/m^3$)	Duration of Exposure	Species	Effects	Reference
2.0 average Range 0.7-5.9	9.5 years occupational exposure	Human	Confirmed case of beryllium disease. Beryllium registry.	National Institute for Occupational Safety and Health, 1972 (113.)
5-650	Acute occupational exposure—30 minutes	Human	Decreased vital capacity, pneumonitis, bronchitis	Eisenbud, et al., 1948 (107.)
34 ($BeSO_4$)	7 hr/d, 5 d/wk for 72 weeks	Rat	Lung tumors first occurred after 9 months exposure; 100% incidence at 13 months exposure	Reeves, et al., 1967 (115.)
35 ($BeSO_4$)	8 hr/d, 5 d/wk 9 hr on Saturday for 6 months	Rat	Pulmonary lesions started on month 6.	Schepers, et al., 1957 (116.)
55	6 hr/d, 5 d/wk	Rat	Pulmonary lesions (focal and randomly scattered) after 9 months	Vorwald and Reeves, 1959 (121.)

and effects in other chronic cases has been lacking because of inadequate analytical capabilities at the time of exposure. Therefore, a dose-response relationship of beryllium exposure at low levels cannot be developed.

Several investigators have conducted epidemiological studies of occupational exposures to beryllium, attempting to correlate length of employment in beryllium occupations and cause-specific mortality. Results of these studies are inconclusive. Mancuso (112.) reported an inverse relationship between length of employment and lung cancer as well as for total mortality. Similar findings were reported by other investigators (110.). Mancuso's results did not establish the carcinogenicity of beryllium in humans, but mentioned the possibility. Reeves (114.) summarized beryllium toxicity thus, "the sum of evidence, at least thus far, favors the view that humans, like the guinea pig, are susceptible to berylliosis but resistant to beryllium cancer".

Although the carcinogenicity of beryllium is suspect, the etiology of chronic beryllium disease or "berylliosis" is well established. Sterner and Eisenbud (118.) hypothesized that chronic beryllium disease was the result of antigen-antibody interaction in the affected tissue. Deodhar et al. (106.) also reported strong evidence for the existence of cellular immune reactivity to beryllium in patients with chronic beryllium disease.

The question then arises, at what level of exposure will an individual develop a reaction leading to chronic beryllium disease? Sensitivity differences between sexes and host variability (114.) makes it difficult to establish this value. Neighborhood cases of chronic beryllium disease were reported at ambient air concentrations of 0.01 $\mu g/m^3$. Lieben et al. (111.) questioned these cases and established exposures to beryllium in excess of the ambient concentrations for each of these "neighborhood cases". The National Institute for Occupational Safety and Health (113.) concluded that "it has yet to be definitely established whether ambient air contamination alone, at a distance from a manufacturing/fabricating plant, can cause chronic beryllium disease".

Ecological effects of beryllium have been studied in a limited way, most of the work being associated with laboratory toxicology studies. Thus, the studies included in the immediately available literature deal primarily with laboratory animals.

Stokinger et al. (119.) pointed out that the response to relatively high dosages of beryllium (1000 $\mu g/m^3$ air) is species specific. Respiratory exposure to equal concentrations of beryllium in six different animals produced a wide range of effects (120.). Beryllium concentrations lethal to rats produced no functional changes in rabbits, although post mortem examinations of rabbits found pulmonary lesions.

2.1.3 Asbestos

The proposed de minimis level for asbestos is 1 $\mu g/m^3$, 1-hour average. The health effects from respiratory exposure to asbestos have been well documented for occupational environments (126.) and, to a limited extent, nonoccupational environments (125.). Health effects from asbestos exposure have included diffuse interstitial fibrosis, mesothelial malignancies, and cancer of the lung and gastrointestinal tract.

Dose-response curves for asbestos exposures and cancer of the lung and digestive tract (128.) have been developed. Exposure to asbestos concentrations of 125 mppcf-years* has been associated with excessive cancer deaths (125.). Murphy (124.) reported asbestos exposures to 60 mppcf-years would result in diffuse interstitial fibrosis. Individual susceptibilities and other confounding factors may also play a role in disease incidence as latency periods for lung cancer have ranged from 3.5 to 37 years.

The review of available literature revealed several methods of analyses and reporting of asbestos exposure which are not readily interconvertible. For example, occupational exposures to asbestos were reported as millions of particles per cubic foot (mppcf) or fibers per cubic centimeter greater than 5 μm in length, whereas the de minimis level is a mass concentration measurement in $\mu g/m^3$. The National Institute for Occupational Safety and

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*Mppcf-years: Millions of particles per cubic foot-years are computed by multiplying the asbestos level (mppcf) at each job and time period by years at the job and summed across all jobs. The total cumulative exposure is thought of as mppcf-years (122.). It should be noted that such exposures are occupational, 8 hours per day, and not continuous as in community exposures.

Health (126.) considered this conversion problem and concluded that a general conversion factor for equating $\mu g/m^3$ to mppcf could not be developed. Inherent differences in asbestos type and operation of the plant generating the asbestos would result in conversion factors ranging from 11 to 108,000 for estimating the number of fibers per nanogram. Furthermore, the majority of health effects data are from occupational exposures using fiber number concentrations. Fiber size and shape are important factors in producing tumors, with fibers less than 0.5 μm in diameter most active (126.).

Asbestos fiber length has been considered important in initiating fibrosis, but Selikoff and Lee (129.) pointed out that it cannot be said with any confidence that fibrogenicity drops to negligible proportions at fiber lengths of 5 μm or 1 μm. The authors speculated that smaller fibers may also be responsible for fibrotic and mesotheliomatous reactions. Other confounding factors affecting disease induction include cigarette smoking (129.).

The available health effects data for developing dose-response curves are available but in units of measure as particle counts and not mass concentrations. The dose response information is further limited in its application since it was generated from health workers occupationally exposed and not from continuous exposure to the general population.

Asbestos has been reported to cause pulmonary fibrosis in wild and domesticated animals living in the vicinity of asbestos mines or factories. High concentrations are implied but dose-response information is not available (123.).

Available information on the effects of asbestos to nonhuman organisms is of recent origin and involves laboratory animals exposed to high dosages. Physiological reactions in rats include formation of malignant neoplasms as well as various gross morphological changes in the lung for chronic exposures (2 years) to milled asbestos at approximately 49 mg/m^3 (fiber concentration of 0.08 to 1.82 percent). Mice, gerbils, and guinea pigs exhibited similar morphological changes, but no neoplasms were observed under similar exposures (127.).

As with man, the literature generally supports the assumption that fiber length, fiber concentration, and chemical origin or type of asbestos mineral influences the response of an organism exposed to asbestos. In fact, literature reporting asbestos exposure is infrequently reported in $\mu g/m^3$, but rather as fiber concentration or total "asbestos" concentration including nonfibrous pseudomorphs and other allied chemical species. Furthermore, the interconversion of these various types of measurements is a technically difficult problem as explained above. No information was found concerning field-observed effects of asbestos on plants and animals.

2.1.4 Fluorides

The proposed de minimis level for fluorides is 0.01 $\mu g/m^3$, 24-hour average. The health effects data in Table 2-3 relate to occupational and community respiratory exposures to fluorides in or near aluminum smelters and phosphate fertilizer plants. The populations concerned were subject to concomitant exposure to other compounds associated with the respective industries.

Many community studies have monitored dental fluorosis in children as an evaluation of respiratory fluoride exposure. Dental fluorosis, or mottled enamel, is a result of functional changes preceding the eruption of a tooth. Consequently, chronic fluoride exposure will result in mottled enamel in children under the age of five to eight years, but can be tolerated without effects in adults. Leloczky (109., cited in 136.), reported fewer dental caries than expected in children exposed to 0.03 to 0.06 mg/m^3 fluoride particulates in air. Sadilova (185., cited in 136.) supported this finding, but noted an increase in the incidence of mottled enamel in children exposed to 0.03 to 0.56 mg/m^3 in air. Agate et al. (131., cited in 136.), also observed fewer dental caries in children living near an aluminum production plant, but noted a slight increase in very mild mottling of tooth enamel associated with respiratory exposure to 0.045 to 0.048 mg/m^3 fluorides.

Elkins (132.) reported nosebleeds and sinus trouble in welders exposed to 0.7 mg/m^3 hydrogen fluoride. Midttun (108., cited in 136.), observed an allergic asthma reaction of unknown etiology in aluminum plant workers

TABLE 2-3. HEALTH/ECOLOGICAL EFFECTS OF POPULATIONS EXPOSED TO FLUORIDES IN AIR

Exposure Concentration	Duration of Exposure	Species	Effects	Reference
0.54-0.66 μg/m^3	Continuous	Corn (*Zea mays*)	Mild leaf symptoms; Chlorotic streaking on tips and margins of leaves.	Pack and Sulzbach, 1976 (142.)
0.55 μg/m^3	Continuous	Strawberry Marshall Var.	Achenes and underlying receptacle tissue at the apical end of fruit did not develop.	Pack, 1972 (141.)
0.64 μg/m^3	Continuous	Soybean (*Glycine max*)	Significant reduction in number of pods, weight/seed, stem length, significant increase in dry weight of stems and leaves.	Pack and Sulzbach, 1976 (142.)
0.76 μg/m^3	Continuous 40 days	Gladiolus, var. Snow Princess	39% increase in oxygen uptake over controls (increase in respiration). Necrosis.	Hill, et al., 1959 (133.)
0.98 μg/m^3	Continuous 24 hr	Ponderosa pine (*Pinus ponderosa*)	Chlorosis of young needles.	Adams, et al., 1956 (130.)
1.6 μg/m^3	Continuous 7 days	Corn (*Zea mays*)	A mean of 1.9% of total leaf area affected by necrosis.	Hitchcock, et al., 1964 (134.)
2.0 μg/m^3	Continuous	Corn (*Zea mays*)	Seed production completely inhibited.	Pack and Sulzbach, 1976 (142.)
4.3 μg/m^3	Continuous	Oat (*Avena sativa*)	Delay of maturation; significant increase in dry weight of stems and leaves.	Pack and Sulzbach, 1976 (142.)
4.7 μg/m^3	Continuous	Sorghum (*Sorghum vulgare*)	85% reduction in seeds; 30% reduction in seed weight (weight/seed); increase in dry weight of stems and leaves.	Pack and Sulzbach, 1976 (142.)
5.0 μg/m^3	Continuous	Wheat (*Triticum aestivum*)	No significant difference from controls in seed production, seed weight, dry stems and leaf weight. Trace of leaf tip dieback noted after 10 weeks.	Pack and Sulzbach, 1976 (142.)
8.2 μg/m^3	Continuous	Wheat (*Triticum aestivum*)	50% reduction in number of seeds produced; 18% reduction in weight/seed; Decrease in dry stem and leaves weight.	Pack and Sulzbach, 1976 (142.)

TABLE 2-3. HEALTH/ECOLOGICAL EFFECTS OF POPULATIONS EXPOSED TO FLUORIDES IN AIR (continued)

Exposure Concentration	Duration of Exposure	Species	Effects	Reference
10.4 $\mu g/m^3$	Continuous	Strawberry Marshall var.	Severely restricted fruit development. Approximately 50% decrease in weight/fruit. Significant reduction in percentage of flowers that developed into fruit. Chlorosis of leaves; Marginal necrosis.	Pack, 1972 (141.)
40 $\mu g/m^3$	Continuous 7 days	Soybean (Glycine max)	Average of 34.3% increase in respiration.	Yu and Miller, 1967 (149.)
0.03-0.11 mg/m^3	Single exposure	Human	Perceptible odor concentration.	National Institute for Occupational Safety and Health, 1976 (140.)
0.045-0.048 mg/m^3	Community exposure – continuous	Human	Slight increase – very mild mottling of tooth enamel compared to control. Teeth of children near plant appeared less prone to caries.	Agate, 1949 (131.), cited in (136.)
0.03-0.06 mg/m^3	Community exposure – continuous	Human	Children with slightly less caries than normal and excreted $\leq$6.6 mg F/l in urine.	Leloczky, 1970 (109.), cited in (136.)
0.03-0.56 mg/m^3	Community exposure – continuous	Human	Incidence of mottled enamel: Exposed 31.0-37.5%. Control 2.1%. Incidence of dental caries: Exposed 10.8-24.5%. Control 37.5%.	Sadilova, 1957 (185.), cited in (136.)
0.09-0.90 mg/m^3	Community exposure – continuous	Human	Slight dental fluorosis – 58%. Moderate dental fluorosis – 8%. Severe dental fluorosis – 1%.	Khyngin and Shamsutdinova, 1970 (139.), cited in (136.)
0.14 mg/m^3	Community exposure – continuous	Human	No significant differences in clinical observations between exposed and control.	Balazova, 1971 (212., 223.) Balazova, et al, 1970 (224.) Hluchan, et al, 1968 (225.) Balazova & Lipkova, 1974 (226.) Lezovic & Balazova, 1969 (227.) cited in (136.)
0.7 mg/m^3	6h	Human	Welders exposure to AP-Nosebleeds.	Elkins, 1959 (132.)
2.5 mg/m^3	Occupational – Aluminum plant workers	Human	Sinus trouble Osteosclerosis	Hodge and Smith, 1977 (136.) Kaltreider, 1972 (138.)
1-2 mg/m^3	Occupational – Aluminum plant workers	Human	Nausea, headache, irritation of conjunctiva and respiratory passages. 54 cases allergic asthma observed over 5 years. Allergen unknown fluoride compound. Concomitant exposure to organic tars, dust borne fluorides, HF, AlF_3, cryolite, Al_2O_3, SO_2.	Midttun, 1960 (108.), cited in (136.)

exposed to 1 to 2 mg/m^3 particulate fluorides. Nausea, headache, irritation of conjunctiva and respiratory passages were also observed. Hodge and Smith (136.) and Kaltreider (138.) noted osteosclerosis in aluminum plant workers exposed to 2.5 mg/m^3 fluoride particulates in air.

Study of the health effects of exposure to low concentrations of atmospheric fluorides has centered on dental effects in children. The ability of fluorides to prevent dental caries has been noted; indeed, the addition of fluorides to drinking water is recommended to prevent dental caries.

The primary ecological effect of fluorides is on vegetation. Gaseous fluorides enter the leaves of vegetation primarily through the stomata, the primary site of accumulation being leaf tips or margins (137.). The visible symptoms of fluoride toxicity vary according to the type of plant, but seem to be relatively consistent. The initial symptoms of most harbaceous plants is chlorosis, starting at the leaf margins of elongating leaves; usually this results in necrosis. In many of the grasses including corn and sorghum, chloritic flecks appear scattered at the tips and upper margins of the middle-aged leaves.

Ponderosa pine is very susceptible to fluoride toxicity. An atmospheric exposure of 0.98 μg/m^3 for 24 hours produced chlorosis of the immature needles, which turned to a light brown or reddish brown at the tips. This discoloration may be interrupted by dark bands, which may indicate intermittent exposures (148.).

The work of Pack (141.) and Pack and Sulzbach (142.) indicated that damage to a plant may result before visible symptoms occur. For example, strawberry bushes grown in a continuous exposure to 5.0 μg/m^3 air (hydrogen fluoride) exhibited a significant decrease in fruit development and fruit weight compared to controls, yet showed no signs of chlorosis (141.).

Animals are exposed to fluorides principally from ingesting contaminated forage or from feed supplements. The most frequently encountered symptoms are dental lesions. In sheep, ingestion of 10,000 mg/m^3 fluorides in water caused decreased wool production and dental lesions (143.). Fluorides added to feed at a concentration of 2.0 mg/kg caused slight mottling and wear on the fourth incisor of dairy cattle (147.). Stoddard et al.(145.) fed dairy cattle 2.08 mg/kg of fluoride in feed (109 ppm) and found reduced lactating ability but not a significant decrease in overall production of milk. When fed 1.17 mg/kg fluoride in feed (55ppm), reduced feed consumption and reduced lactating ability were noted. But again, there was no significant decrease in total milk production (146.).

One problem in a literature study is to generalize the results of experiments in which fluorides added to feed or water are compared to results where animals forage naturally contaminated feed. Shupe et al. (144.) fed groups of dairy heifers food supplemented with sodium fluoride and calcium fluoride as well as the fluoride contaminated hay, and found that the naturally contaminated hay was as toxic as the sodium fluoride supplement. In addition, Hobbs and Merriman (135.) found that hay contaminated with fluoride from an aluminum smelter was somewhat less toxic than sodium fluoride supplemented food.

There is evidence that a lag period may exist before physiological expression of fluoride toxicity. Suttie et al. (147.) found a two to five year latent period between the time dental lesions were noted and the development of other physiologic effects including depression of milk production. Thus, he suggests that fluoride toxicity is a function of exposure (time) and amount of ingestion.

2.1.5 Sulfuric Acid Mist

The proposed de minimis level for sulfuric acid mist is 1 $\mu g/m^3$, 24-hour average. A comprehensive review of the human health effects from sulfuric acid mist published by the National Institute for Occupational Safety and Health (NIOSH) was the source for much of the effects data described below (162.).

The reported health effects from respiratory exposure to low concentrations (Table 2-4) report different effects as explained in the following narrative.

TABLE 2-4. HEALTH/ECOLOGICAL EFFECTS OF POPULATIONS EXPOSED TO SULFURIC ACID MIST IN AIR

Concentration (mg/m^3)	Duration	Species	Effects	Reference
0.07 (0.1 µm dia) 0.1 (0.3 µm dia) 0.12 (0.7 µm dia) 0.07 (1.0 µm dia) 0.22 (2.5 µm dia)	1 hr	Guinea pig	Increase pulmonary flow resistance percentage: 32 41 43 14 18	Amdur, et al., 1975 (151.)
0.35	5-15 min	Human	Increased respiration rate, decreased maximum inspiratory and expiratory air flow	Amdur, et al., 1952 (153.)
0.4	10 sec	Human	Conditioning of electrocortical reflex	Lewis, et al., 1972 (158.)
0.5	5-14 days	Guinea pig	Slight lung irritation	Bushtueva, 1962 (155.)
0.6-0.85	Unknown	Human	Perception of odor and irritation of mucosa	Lewis, et al., 1972 (158.)
0.8-16.6	Occupational	Human	Etching of dental enamel	Malcolm and Paul, 1961 (159.)
2.9	60 min	Human	Coughing, some bronchoconstriction rales	Sim and Pattle, 1957 (166.)
>4.0 (0.6, 0.9, and 9.0 µm dua)	18-140 days	Guinea pig	Greatest pulmonary pathology occurred at 0.9 µm diameter exposure; foci of pulmonary damage changed with varying particle size.	Thomas, et al., 1958 (168.)
8 (-1 µm dia)	8-72 days	Guinea pig	Increased time of exposure did not increase mortality; suggests concentration more important than duration.	Amdur, et al., 1952 (152.)
20	7 hr/day for 13 days	Rabbit (New Zealand white)	Slight maternal toxicity (none at 5 mg/m^3); no teratogenicity or fetal toxicity	Murray, et al., 1979 (161.)
20	7 hr/day for 9 days	CF-1 mice	Same as above	
87-1600 (<2 µm dia)	NA	Rabbit Rat Mouse Guinea pig	Species sensitivity to H_2SO_4 particles compared; sensitivity increases: Rabbit < Rat < Mice < Guinea pig	Treon, et al., 1950 (221.)

TABLE 2-4. HEALTH/ECOLOGICAL EFFECTS OF POPULATIONS EXPOSED TO SULFURIC ACID MIST IN AIR (continued)

Concentration (mg/m^3)	Duration	Species	Effects	Reference
OTHER MEASUREMENTS				
ph 3.2, 0.9 mm drop size	6 days/wk	Halo blight on kidney beans	Pathogen inhibition (varying percent related related to life cycle stage)	Shriner, 1977 (165.)
		Fusiform rust on willow oak	Pathogen inhibition (86 percent)	
		Kidney beans	SEM observed extensive erosion of cuticular waxes (therefore, 3.2 pH may inhibit host invasion but cuticular erosion leaves plant more susceptible to invasion post exposure).	
1.7 μm aerodynamic diameter of 18 M sulfuric acid	10 hrs/day for 14 days	4- to 6-wk-old soybean seedlings	None observed with scanning electron microscope or human eye	Wedding, et al., 1979 (170.)

The health effects from respiratory exposure to sulfuric acid mist include irritant effects on mucous membranes and chemical corrosion of dental enamel. Amdur et al. (153.) reported changes in respiratory rates and respiratory flow from exposure to 0.35 mg/m^3. The exposure tests were conducted on human volunteers of various ages. The authors noted that asthmatics, cardiac patients, and other less healthy persons in the general population may be more susceptible to sulfuric acid mist exposure. NIOSH (162.) reported similar results by Morando (160.), but questioned the validity of the findings at these concentrations. Sackner et al. (164.) supported the NIOSH conclusions showing no respiratory resistance at sulfuric acid concentrations of 0.01 to 1.0 mg/m^3. Toyama and Nakamura (169., cited in 162.) demonstrated pulmonary airway resistance in humans at exposures of 0.01 to 0.1 mg/m^3, but concluded that concomitant hydrogen peroxide and sulfur dioxide exposure had produced a synergistic effect.

Earlier, Lewis et al. (158.) extensively reported the sensory and central nervous system studies in the USSR and noted conditioned reflex responses and perception and irritation thresholds in humans exposed to atmospheric concentrations of 0.4 and 0.6 to 0.85 mg/m^3, respectively. Malcolm and Paul (159.) reported etching of dental enamel from occupational exposures to 0.8 to 16.6 mg/m^3 sulfuric acid mist. Other studies have noted etching of dental enamel but accurate monitoring measurements were lacking (167., 154.).

NIOSH (162.) also noted one study by Raule (163.) which reported worker acclimation to inhalation of sulfuric acid mist. Conversely, Sim and Pattle (166.) noted long-lasting bronchitic symptoms in two male volunteers. Contradictions of effects at similar concentrations may be due to variance in relative humidity, temperature, and particle size (150., 156., 162., 166.).

On the other hand, it must be remembered that all studies described above were either occupational or human volunteer studies of health persons. It is possible, as noted by Amdur et al. (153.), that less healthy persons in the general population may be more susceptible to sulfuric acid mist exposures. Epidemiological studies to support this relationship and identify a dose-response relationship are lacking.

From the viewpoint of nonhuman effects, there has been extensive testing of the effects of sulfuric acid aerosol exposure on laboratory animals and on selected plant species; however, the lowest known value reported in the literature as having a biological effect is 0.07 mg/m^3 (151.).

In Table 2-4 selected literature references for acute or chronic biological effects of sulfuric acid aerosol are presented. Damage from sulfuric acid aerosol is species-specific (221.). Particle size has a major influence on both the degree of damage and the specific places of damage in the pulmonary system (168., 151.). However, insufficient information is available to establish a lower limit of effect. Because of the powerful hygroscopic nature of concentrated sulfuric acid, it is likely that any exposure results in some effect on biological tissues (157.).

Waxy coatings on many plants are somewhat protective, though erosion of these layers begins with initial exposure to sulfuric acid (170., 171., 172.). Increased exposures result in tissue damage from drying, heating, and charring. On the other hand, sulfuric acid aerosol exposure appears to be associated with a slight increase in resistance to parasite attack, probably the result of either damage to the parasite or substrate changes which, in turn, do not provide favorable conditions for the parasite/host relationship (165.).

2.1.6 Vinyl Chloride

The proposed de minimis level for vinyl chloride is 1 µg/m^3, maximum value. Toxicological experience with this compound came as a result of occupational health studies which identified an excess incidence of angiosarcoma of the liver in vinyl chloride workers (175.). Vinyl chloride was previously considered non-toxic and therefore exposure was not of great concern. Consequently, adequate personal monitoring data do not exist to allow an accurate estimate of worker exposure and cancer risk.

Several researchers have correlated length of exposure measured as years of work in vinyl chloride plants to occupational diseases including angiosarcoma of the liver (174., 175., 184.), respiratory and brain cancers, cancer of other unspecified sites, and chromosome aberrations (177.).

Other health effects observed include nervous manifestations (euphoria), cardiovascular manifestations (arterial hypertension), Raynaud's syndrome (abnormal sensitivity to cold), digestive problems (hepatomegaly), respiratory manifestations, skin irritations, endocrine alteration, hematologic changes, and bone changes (acroosteolysis) (179., 180., 183., 186.).

Several community epidemiological studies have been conducted to correlate proximity to a production facility and various health effects. For example, Infante (178.) noted an excessive number of congenital malformations in communities with polyvinyl chloride production facilities. Ambient concentrations of vinyl chloride during the study period were not given; therefore, no association between vinyl chloride exposure and congenital malformations can be stated.

Edmonds et al. (176.) conducted a community case-control study of the possible relationship between congenital central nervous system malformations and exposure to vinyl chloride monomer emissions from a local plant. Although central nervous system malformations were significantly higher than the United States rates, no correlation was found with occupation of parent or residential proximity to the plant site. The authors suggest that vinyl chloride may be one of several pollutants emitted from nearby plants which may be responsible for the high rates.

NIOSH (181.) concluded that there is probably no threshold for carcinogenesis from vinyl chloride exposure, although it is possible that at very low concentrations the latency period may be extended beyond the life expectancy. This implies that setting a low enough exposure level for vinyl chloride may decrease cancer incidence, but data thus far have come from healthy workers occupationally exposed 8 hours per day. Thus, setting a safe level for persons not occupationally exposed must consider those most susceptible to disease.

Basuk and Nichols (173.) best summarized the vinyl chloride data by stating that because of the extremely high vinyl chloride concentrations in plants with little or no reliable monitoring facilities, because of personnel turnover and lack of medical records and because of unknown effects of other contaminants used in the process which may be carcinogenic, it is impossible to determine the shape of the human dose-response curves except in a rough qualitative manner.

The relatively recent understanding of the hazard of vinyl chloride to man has resulted in studies using laboratory animals to establish dose-response relationships. Early testing at exposures assumed to be at nontoxic levels has resulted in carcinogenesis. It is believed that subsequent testing has been conducted at lower levels, but these findings have apparently not reached the open literature, and, consequently, are not accessible.

Vinyl chloride is carcinogenic in a number of laboratory species including mice, rats, and hamsters. Mammary carcinomas can be induced in laboratory animals by exposure to one ppm or less of vinyl chloride (173.). Repeated daily exposures in both rats and mice at 50 ppm are carcinogenic (187.). Also, incidence of angiosarcoma and nephroblastomas appear to be dose related in the lower range of exposures (182.).

Information is not available on either chronic or acute effects of exposure of vinyl chloride to natural populations.

2.1.7 Hydrogen Sulfide

The proposed de minimis level for hydrogen sulfide is one µg/m^3, one-hour average. Much of the available health effects data for hydrogen sulfide were derived from acute occupational exposure studies of concentrations greater than five mg/m^3 (see Table 2-5). Community studies of hydrogen sulfide exposure have also been reported but exposures were much higher than the de minimis levels. Thus, the major effects at the de minimis concentrations are psychophysical responses to odors.

The odor threshold has been variably reported at one to 45 µg/m^3 by Miner (192.) and 0.65 µg/m^3 by Leonardos et al. (191.). Differences in odor thresholds can be explained by variations in the methods and statistical analyses used to determine the threshold level and inherent variation in the study population (193.). The National Research Council (193.) reviewed the psychophysical factors of hydrogen sulfide exposure and concluded that one cannot depend on adaptation to reduce awareness of odorous pollution. The National Research Council noted that sociological factors (such as age,

TABLE 2-5. HEALTH/ECOLOGICAL EFFECTS OF POPULATIONS EXPOSED TO HYDROGEN SULFIDE IN AIR

Exposure Concentration, µg/m^3	Duration of Exposure	Species	Effects	Reference
1-45	—	Human	Odor Threshold	Miner. 1969 (192.)
18	12 hr/d 3 months	Rat	Motor chronaxie abnormalities	Duan, 1959 (189.)
42	Continuous	Sugarbeet Lettuce	Increased yield	Natl. Res. Council, 1979 (193.)
400	2 months	Human	Community exposure—Terre Haute, Indiana. Nausea, loss of sleep, abrupt awakening, breathlessness. H_2S range 30-11000 µg/m^3	Illinois Institute for Env. Quality, 1974 (190.)
420	Continuous	Ponderosa pine	Tip burn visible after 8 weeks	Natl. Res. Council, 1979 (193.)
420	Continuous	Seedless grape	Detectable damage, lesions on leaves	As above (193.)
420	Continuous	Alfalfa	Successive harvests showed yield reduction	As above (193.)
5,000	Unknown	Human	Occupational exposure. Conjunctival and corneal irritation. *Concomitant* CS_2 *exposure.* H_2S range 5,000-20,000 µg/m^3	Masure, 1950, (228.), cited in (193.)
10,000	12 hr/d 3 months	Rat	Mild irritation of tracheal, broncheal mucosa, lower weight gain, motor chronaxie abnormalities, abnormal cerebral cortex dendrites.	Duan, 1959 (189.)
15,000	6-7 hr	Human	Occupational exposure. Eye irritation	Nesswetha, 1969 (229.),cited in (194.)
15,000	5d	Mouse	Anorexia	Hays, 1972, (230.),cited in (194.)
28,000	90d	Monkey	Weight loss, increased blood amylase and alkaline phosphatase activities	Sandage, 1961 (195), cited in (194.)
28,000	8 hr/d	Human	Occupational exposure. Fatigue, decreased libido, anorexia, dizziness, eye and respiratory tract irritation.	Ahlborg, 1951 (188.)

sex, and socioeconomic status) affect odor complaints. They concluded there is no evidence that the experience of malodor per se produces disease but noted that poor health may increase the displeasure or at least the frequency of complaints about odors.

Community exposure studies in Terre Haute, Indiana conducted by the Illinois Institute for Environmental Quality (190.), observed various psychological disturbances from atmospheric hydrogen sulfide concentrations of 400 μg/m^3. Nausea, loss of sleep, abrupt awakening, breathlessness, headaches, abdominal cramps, diarrhea, choking, coughing, eye irritation and acute asthma attacks were described. The Institute suggested that low concentrations of hydrogen sulfide posed special dangers to individuals with neart or lung disease (190., 228., cited in 193.).

Studies of occupational exposure have generally concentrated on effects at levels greater than 5000 μg/m^3. Health effects from occupational exposures included eye and respiratory tract irritation and brain damage. The existence of a discrete clinical chronic poisoning from hydrogen sulfide has been questioned (194., 193.), with some indication that the chronic poisonings are actually recurring acute or subacute toxic exposures.

Acute effects have not been included in Table 2-5 since these effects occur at concentrations greater than 700 mg/m^3. At such concentrations, respiratory distress, nervous system effects, and eventual paralysis of breathing occur (194.).

The environmental effects of hydrogen sulfide, as assessed through laboratory experiments, are both varied and species specific. At low levels (4 μg/m^3 in air) continuous exposure produced an increased yield on sugar beets and lettuce (193.). Concentrations an order of magnitude higher, however, caused tip burn on ponderosa pine, and lesions on the leaves of seedless grapes (193.). Effects on animals show up with concentrations in the 10,000 μg/m^3 range and above. Symptoms range from mild irritation of trachea and broncheal mucosa to anorexia and weight loss.

2.1.8 Methyl Mercaptan

The proposed de minimis level for methyl mercaptan is 0.5 $\mu g/m^3$, one-hour average. Toxicological data are limited to a few cases.

Shults et al. (198.) described an acute respiratory exposure to methyl mercaptan (methanethiol) in a 53 year old black male. The worker was engaged in salvaging metal cylinders and was instructed to empty tanks containing methyl mercaptan. The worker was presumably exposed to high atmospheric concentrations of the compound, although personal monitoring was not available. Acute, severe hemolytic anemia and methemoglobinemia developed. Deep coma persisted and the victim died 28 days after exposure. The authors concluded that the likely mechanism of the hemolysis was an oxidant effect of methyl mercaptan in a person deficient in erythrocytic glucose-6-phosphate dehydrogenase (G-6-PD), an inherited deficiency.

Fairchild and Stokinger (196.) and Key et al. (197.) described local and systemic effects in humans from respiratory exposure to methyl mercaptan. Observed effects included irriation of skin, eyes, and mucous membranes. The toxic effect of methyl mercaptan is similar to that of hydrogen sulfide with central nervous system depression resulting in respiratory paralysis. Although personal exposure data and ambient measurements of methyl mercaptan were not given, the above effects probably occur at excessive levels, several orders of magnitude higher than the proposed de minimis level.

Leonardos et al. (191.) reported an odor threshold for methyl mercaptan of 0.0021 ppm (4.1 $\mu g/m^3$). Verschueren (199.) reported a threshold odor concentration of 0.044 $\mu g/m^3$. The differences in the two odor threshold values reported may be explained by methods of study, sensitivity of observers to the odor, and different types of odor thresholds reported. For example, the study by Leonardos et al. (191.) reported an odor threshold which can be recognized by all panel members (Population Identification Threshold 100 percent) whereas the value reported by Verschueren (199.) was an absolute perception threshold.

Available information on the toxic effects of methyl mercaptan on nonhumans is limited to a few high dosage experimental animal studies. The concentration which caused 50 percent of experimental rats to become comatose was determined to be 0.16 percent by volume (200.). The concentration of methyl mercaptan lethal to rats after 10 to 20 minutes exposure was determined to be 1.0 percent by volume (231.).

2.1.9 Dimethyl Sulfide

The proposed *de minimis* level for dimethyl sulfide is 0.5 $\mu g/m^3$, one-hour average. This level was established primarily to control odors. Specific information on the human health effects of dimethyl sulfide were not found in the available literature. The following discussion deals with the odor properties of the compound.

Leonardos et al. (191.) reported an odor threshold of 0.001 ppm (2.6 $\mu g/m^3$) for dimethyl sulfide. Verschueren (199.) reported an absolute perceptible limit of 0.4 ppb (1.0 $\mu g/m^3$).

Dimethyl sulfide is one of four total reduced sulfur (TRS) compounds for which *de minimis* levels were proposed. These TRS compounds are characterized as highly odorous, generally considered repugnant or malodorous. The National Research Council (218.) noted physiologic and morphologic changes occur in animals from exposure to odorants. These effects are different from toxic effects. Similar manifestations from exposure to odorous pollutants are suggested in humans. The Council noted that the impact of these changes on human health has yet to be established, but warrant immediate study.

No information was available in the immediate literature concerning field-observed effects of dimethyl sulfide on nonhumans. Only data on high dosage, experimental animal studies were available. Ljunggren and Norberg (231.) state that a 5.4 percent by volume concentration (140,000 mg/m^3) of dimethyl sulfide is lethal to rats after a 10 to 20 minute exposure. Zieve et al. (200.) report that the inhalation dose at which 50 percent of rats become comatose is 9.6 percent by volume (243,040 mg/m^3).

2.1.10 Dimethyl Disulfide

The proposed *de minimis* level for dimethyl disulfide is 2 $\mu g/m^3$, one-hour average. This level was established primarily to control odors. Toxicological information for dimethyl disulfide is sparse, with only limited short-term studies on animals and no data for human health effects available. Thus, the discussion will be limited to the odor properties of the compound.

Verschueren (199.) reported two different odor thresholds for dimethyl disulfide: a threshold odor concentration of 0.005 mg/m^3 and a 50 percent recognition threshold of 5.6 ppb (21.5 $\mu g/m^3$). Berglund (219.) studied the effects of sulfurous compound mixtures on odor intensity and noted additive and interactive components of mixtures. For example, a field investigation of a pulp mill indicated that selective elimination of several sulfur compounds including dimethyl disulfide would not necessarily reduce the odor strength of the effluent. Indeed, the author noted that a slight increase in odor intensity may result from selective elimination of hydrogen sulfide, methyl mercaptan, dimethyl disulfide, and dimethyl sulfide.

Dimethyl disulfide is a naturally occurring compound produced from aerobic or anaerobic activity in soils and organic matter (232., 233., 234.). Dimethyl disulfide residues have been confirmed in human blood, urine, and respiratory gas (235., 236., 237.). Gage (238.) reported symptoms of lethargy, respiratory difficulties, and low weight gain in rats exposed to 250 ppm dimethyl disulfide in air. Respiratory exposure to 100 ppm dimethyl disulfide did not elicit a toxic reaction, after six-hours exposure. Kadota and Ishida (234.) reported inhibition of *Aphanomyces euteiches* (Pea root rot) at dimethyl disulfide concentrations as low as 20 ppm.

2.1.11 Carbon Disulfide

The proposed *de minimis* value for carbon disulfide is 200 $\mu g/m^3$, one-hour average. Toxicological experience with carbon disulfide in humans has been limited to occupational exposures in the viscose rayon industry where concomitant exposure to hydrogen sulfide occurs. A comprehensive review of human health effects from respiratory exposure to carbon disulfide published

TABLE 2-6. HEALTH/ECOLOGICAL EFFECTS OF POPULATION EXPOSED TO CARBON DISULFIDE IN AIR

Exposure Concentration, (mg/m^3)	Duration of Exposure	Species	Effects	Reference
			Carbon Disulfide Alone	
0.08	10-15 minutes	Human	Disturbed rate of execution of assigned motor responses	Bokina, et al., 1976 (206.)
0.09	10 minutes	Human	CNS effects - visual center of brain	Bokina, et al., 1979 (205.)
0.65	-	Human	Odor threshold	Leonardos, et al., 1969 (191.)
			Carbon Disulfide and Other Chemicals	
1.0 [a] 0.1	160 d	Rat	Inflammation of bronchi, weight changes, increased serum aspartate amino-transferase and blood cholinesterase. Most severe with concomitant exposures.	Misiakiewicz, et al., 1972 (209.), cited in (211.).
1.5-4.2	Unknown	Human	Increase in color and light sensitivity	Gabovich, et al., 1978 (210.)
3-10	9 months Occupational exposure	Human	Hypotension; nervous system excitability	Kramarenko, et al., 1971 (240.), cited in (211.)
9	0.5-30 years Occupational exposure	Human	Retinal degeneration; conjunctival inflammation; color-vision disturbances	Szymankowa, 1968, (213.), cited in (211.)
9-50	4+ years Occupational exposure	Human	Immunologic abnormalities	Kashin, 1965 (241.), cited in (211.).
10	Occupational exposure	Human	Adverse effects—menstruation and pregnancy in exposed workers	Agadzhanova, 1978 (203.)
10	Occupational exposure	Human	Increased digestive tract diseases	Gabovich, et al., 1975 (210.)
15	Occupational exposure	Human	Muscular power diminished, reflexes slowed	Vasilescu, 1972, (239.), cited in (211.).

[a] Concomitant exposure to hydrogen sulfide; see text for limitations of this study.

by the National Institute for Occupational Safety and Health (211.) was relied upon for much of the effects data described below. Carbon disulfide exposure has produced health effects in the cardiovascular, neurologic, and reproductive systems and in the eye (Table 2-6).

The odor threshold for carbon disulfide is 0.21 ppm (0.65 mg/m^3) by Leonardos et al. (191.), but has been reported as low as 0.08 mg/m^3 by Baikov (127) cited in (201.). Lindvall (208.) noted that a concomitant exposure to hydrogen sulfide, nitric oxide, and acid fumes increased the human sensitivity to carbon disulfide. Studies by Berglund (219.) emphasized this finding, noting that exposure to a mixture of sulfur compounds will alter the psychophysical response to the odor. The National Research Council (218.) emphasized the adverse public response to odors of sulfurous compounds and suggested setting acceptable odor limits for compounds other than hydrogen sulfide at ten times the odor threshold.

The lowest concentration eliciting a response to carbon disulfide gas was documented by Bokina et al. (206.). Human volunteers exposed to 0.08 mg/m^3 exhibited disturbed rates of motor responses. Bokina et al. (205.) later described central nervous system effects on the visual center of the brain from exposure to 0.9 mg/m^3 carbon disulfide.

Much of the remaining health effects data presented in Table 2-6 were published by Russian and Eastern European authors who have studied protective and adaptive reactions of carbon disulfide on humans. Kramarenko (240., cited in 211.) observed hypotension and nervous system excitability in viscose rayon workers exposed to three to ten mg/m^3 carbon disulfide in workroom air. Kashin (241., cited in 211.) described immunologic abnormalities in viscose rayon workers exposed to ten to 50 mg/m^3 carbon disulfide in air. Agadzhanova (203.) described adverse effects on menstrual function and pregnancy in female rayon workers exposed to ten mg/m^3 in workroom air. Petrov (242.) cited in (211.), noted an increased risk of spontaneous abortions in female rayon workers exposed to atmospheric concentrations of 27 mg/m^3 carbon disulfide for three plus years. Cardiovascular effects were reported by Gavrilescu and Lilis (243., cited in 211.) in rayon workers exposed for ten years to 20 to 42 mg/m^3 carbon disulfide in workroom air. Arteriosclerotic changes and arterial hypertension were also observed.

Dose response information for carbon disulfide in nonhuman populations is difficult to elucidate, as no published studies of this nature are immediately available.

Laboratory animal studies have been conducted because of the need to better understand the human effects. Respiratory exposure levels have been approximately 1000 mg/m^3. The most frequently occurring effects at this dosage are lethargy and loss of motor control. Effects on reproductive success have also been noted. The relatively new technique of behavioral toxicology has been used to help assess the effects of carbon disulfide (207., 216., 217.). Respiratory exposure to the carbon disulfide affected the operant behavior in pigeons and the aversive threshold in squirrel monkeys.

Some authors (204., 209., 214., 215.) have reported a synergistic effect from exposure to a mixture of carbon disulfide and hydrogen sulfide at levels three orders of magnitude lower than those previously encountered. The possibility of a toxic synergism with these gases is indicated but this type of relationship is hard to confirm. The studies of synergistic effects have definite weaknesses, including the lack of proper controls, insufficient numbers of subjects, lack of statistical reliability and lack of a sufficiently detailed explanation as to procedure and results (211.). These results are of limited reliability.

2.1.12 Carbonyl Sulfide

The proposed de minimis value for carbonyl sulfide is 200 $\mu g/m^3$, one-hour average. Experience with human exposures to carbonyl sulfide is lacking. The review of available literature did not reveal any definitive studies of biological responses to carbonyl sulfide. Therefore, human and ecological effects data are not reported in tabular form. The information presented below describes the available information on carbonyl sulfide. Available information on odor properties of carbonyl sulfide is also described.

Peyton et al. (201.) concluded that carbonyl sulfide and carbon disulfide (see Section 2.1.11) may produce similar effects due to the similar physical and chemical properties. The authors estimated the relative toxicity of carbon disulfide to carbonyl sulfide is a ratio of 2:1 based on the additional sulfur radical on carbon disulfide. They recommended an ambient concentration of 400 $\mu g/m^3$. The National Research Council (193.) concluded that the toxic effect of carbon disulfide was attributed to metabolism to carbonyl sulfide and an unknown form of sulfur. Thus the effects of carbonyl sulfide exposure may be similar to those observed in carbon disulfide exposure. As noted previously (Section 2.1.11), the available data on human effects from carbon disulfide are confounded by the concomitant exposure of hydrogen sulfide. Thus, although the compounds may react similarly in humans, the effects are still uncertain.

The de minimis level of 200 $\mu g/m^3$ for carbonyl sulfide was established primarily to control odors. An odor threshold for carbonyl sulfide was not identified. Wostradowski et al. (202.) reported on carbonyl sulfide research involving Kraft recovery furnaces and concluded that carbonyl sulfide present in concentrations of one to 30 ppm (2.4 to 74 mg/m^3) in flue gas does not significantly contribute to the odor problem. Berglund (219.) in a field investigation of a Kraft pulp mill noted that selective elimination of all the known odorants (hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl, disulfide) would not necessarily reduce the odor strength of the emission. The same may also apply to carbonyl sulfide as supported by Worstradowski et al. (202.).

2.2 ECOSYSTEM EFFECTS

No studies of ecosystem effects of the twelve substances were available in the literature consulted for this study. More exhaustive searches and, especially, interpretation and synthesis of diverse information would be required to elucidate this type of effect. More research could possibly produce, for example, observations on changes in species diversity in the presence of mercury. Other searches and interpretations would develop knowledge of the effect of fluorides on overall plant or primary productivity.

However, it is expected that information on ecosystem effects will be sparse. Only recently has the need been recognized for studies of this type. Consequently, there is not a large body of published knowledge in world literature. Ecosystem parameters, in the absolute sense, are more difficult and costly to measure than toxicological studies using small populations, as reported in Sections 2.1.1 through 2.1.11.

3. NATIONAL EMISSIONS

For the purpose of evaluating the significance of SCCP emissions, a nationwide emission inventory of the pollutants subject to de minimis guidelines for both SCCP and non-SCCP sources is presented in Tables 3-1 through 3-5. A comparison of SCCP versus non-SCCP emissions is presented in Table 3-6. All emission data are for 1974, the most recent year for which information is available. This information is not complete and blanks in the tables indicate where no data were found. Values shown for column totals represent the sums of the reported data, not estimated total emissions.

3.1 TRACE ELEMENTS

Table 3-1 summarizes 1974 national SCCP emissions of trace elements (mercury, beryllium and fluorides). Of the SCCP source categories, Electricity Generation and Industrial Combustion Processes produce the greatest amounts of trace element emissions. Combustion of coal for electricity generation produces over 50 percent of the total mass of emissions for each of the three trace elements.

Non-SCCP sources include industrial processing and waste incineration (see Table 3-2.). Few industrial sources emit beryllium at rates of 100 kg/yr or greater. Fluorides are emitted from several industrial categories, including those associated with ceramic manufacture, phosphorus-based products, and primary metals. Electrolytic production of chlorine generates the largest amount of mercury.

Overall, emissions of beryllium and fluorides from SCCP sources are significantly higher than from non-SCCP. SCCP sources generate nearly all of the beryllium emissions and over 40 percent of fluorides. However, non-SCCP sources generate approximately 75 percent of mercury emissions.

3.2 ASBESTOS

Table 3-3. summarizes national emissions of asbestos. Non-SCCP sources for asbestos emissions are reported in the available data; SCCP source emission are not. The most important non-SCCP sources of asbestos emissions are the production and processing of asbestos. Asbestos production accounts for approximately 75 percent of the total asbestos emisssions nationally.

TABLE 3-1. 1974 NATIONAL EMISSIONS OF TRACE ELEMENTS FROM SCCP

Source Category	Electricity Generation External Combustion (1000 kg/yr)			Industrial External Combustion (1000 kg/yr)			Commercial/Institutional External Combustion (1000 kg/yr)			Residential External Combustion (1000 kg/yr)		
	Mercury	Beryllium	Fluorides	Mercury	Beryllium	Fluorides	Mercury	Beryllium	Fluorides	Mercury	Beryllium	Fluorides
Bituminous Coal										0.0	0.3	13.8
Pulverized Dry Bottom	30.9	145.0	19,996.0	1.4	0.7	2,129.3	0.1	1.6	53.7			
Pulverized Wet Bottom	5.7	27.1	3,716.4	0.7	1.5	418.1	0.0	0.1	1.9			
Cyclone	5.7	27.1	3,716.4	0.2	0.1	126.9						
Stoker	0.3	1.4	190.2	2.5	8.0	1,629.6	0.4	39.0	90.8			
Anthracite										0.0	0.0	0.5
Stoker	0.2	0.6	90.9	0.1	0.1	53.5	0.5	0.3	308.5			
Pulverized Dry Bottom	0.1	0.3	50.9									
Lignite												
Pulverized Dry Bottom		0.4										
Pulverized Wet Bottom		0.1										
Cyclone		0.1										
Stoker		0.1			0.1							
Residual Oil												
Other fired	0.7	3.8	0.2	0.5	2.3	0.1	0.6	2.5	0.1			
Tangentially fired	0.5	2.4	0.1	0.1	0.4	0.0	0.0	0.0	0.0			

Source: Eimutis, et al., 1978(66.)

TABLE 3-2. 1974 NATIONAL EMISSIONS OF TRACE ELEMENTS FROM NON-SCCP

Source Category	Emissions in 1000 kg/yr		
	Mercury	Beryllium	Fluorides
NON-SCCP SOURCES			
Industrial Processes			
Cement		0.1	239.5
Brick Tile Kilns and Dryers			5679.8
Refractories			3408.8
Phosphorus - Elemental			2904.5
Phosphoric Acid - Wet Process			1734.3
Phosphate Rock Drying, Grinding, Calcinating			748.1
Primary Copper Smelting			542.9
Vitreous Kaolin Products			448.3
Flat Glass, Pressed and Blown Glass, and Glass Containers			340.8
Mineral Wool			204.1
Primary Lead Smelting and Refining			181.2
Primary Zinc Smelting			180.9
Triple Superphosphates			162.7
Ammonium Phosphates			120.3
Aluminum Fluoride			94.5
Calcium Phosphate			80.7
Other Fluoride Sources			271.8
Electrolytic Production of Chlorine	137.2		
Potassium Hydroxide	3.2		
Carbon Black Furnace	0.2	0.0	
Municipal Incineration	7.6	0.2	
Incineration of Type '2' Waste	0.9	0.0	
Sewage Sludge Incineration	0.5	0.0	
Coal Refuse Piles, Outcrops and abandoned mines	0.1		
TOTAL NON-SCCP EMISSIONS	150.0	0.3	17300.0

Data Source: Eimutis, et al, 1978(66.).

TABLE 3-3. 1974 NATIONAL EMISSIONS OF ASBESTOS

Source Category	Asbestos (1000 kg/yr)
SCCP Sources	NA[a]
Non-SCCP Sources	
Industrial Processes	
Asbestos Products	485.3
Spinning Asbestos Fibres, Twisting and Winding	65.2
Preparation of Asbestos Fibres	37.8
Carding Asbestos Fibres	27.5
Combing Asbestos Fibres	27.5
Manufacture of Asbestos Products, Weaving	13.7
TOTAL ASBESTOS EMISSIONS	657.0

[a] NA means no information available.

Data Source: Eimutis, et al, 1978(66.).

3.3 SULFURIC ACID MIST

Table 3-4 presents national emissions of sulfuric acid mist for SCCP and non-SCCP source categories. Sulfuric acid emissions were estimated by applying the emission factors in Table 4-6 to a nationwide inventory of total sulfur oxide emissions (reported as SO_2) from Reference 56.

SCCP sources generate approximately 96 percent of all sulfuric acid emissions. Of the SCCP sources, coal combustion by the electric utility sector generates the largest percentage of sulfuric acid emissions. This is due to the large quantity of fuel consumed as well as the high sulfur content of coal. Industrial combustion is less significant than the Electric Utility sector because of the difference in fuels, fuel consumption, and capacity of combustion systems. The Commercial/Institutional and Residential sectors contribute approximately 26 percent of sulfuric acid emissions from SCCP sources. Ninety-four percent of these emissions are from oil combustion.

Emissions from non-SCCP sources are primarily from industrial processing. The production of sulfuric acid accounts for over half of these emissions, and brick and tile kilns and dryers contribute approximately 39 percent.

3.4 VINYL CHLORIDE

Table 3-5 presents national emissions of vinyl chloride. Only non-SCCP sources were reported in the available data. Industrial processing accounts for all emissions of vinyl chloride. The production of polyvinyl chloride and vinyl chloride-ethylene dichloride account for approximately 99 percent of all vinyl chloride emissions nationally.

3.5 TOTAL REDUCED SULFUR AND REDUCED SULFUR COMPOUNDS

Available data sources did not indicate total reduced sulfur and reduced sulfur compound emissions for stationary conventional combustion sources. Non-SCCP source category emissions were primarily from industrial processes (see Table 3-6.). Pollutants are ranked as follows according to total emissions produced by these sources per year:

TABLE 3-4. 1974 NATIONAL EMISSIONS OF SULFURIC ACID MIST

SCCP Source Category	Sulfuric Acid Mist (1000 kg/yr)
Electricity Generation	
External Combustion	
Coal	144,213
Oil	49,885
Internal Combustion	
Oil	
Turbines	190
Reciprocating Engines	56
Industrial Combustion	
External Combustion	
Coal	22,675
Oil	33,559
Internal Combustion	
Oil	
Turbines	169
Reciprocating Engines	70
Commercial/Institutional	
External Combustion	
Coal	2,358
Oil	43,536
Residential	
Coal	2,449
Oil	39,908
TOTAL SCCP EMISSIONS	339,000
Non-SCCP Source Category	Sulfuric Acid Mist (1000 kg/yr)
Sulfuric Acid	7,105.2
Production of Lead Acid Batteries	405.6
Carbonizing Wool Fibers	5.5
Chlorosulfonic Acid	14.1
Salicylic Acid	0.9
Salicyclates-Excluding Aspirin	0.1
Brick and Tile Kilns & Dryers	4,797.5
Chlorosulfonic Acid-Inorganic Acids	26.1
Sulfated Ethoxylates-AEOS	20.0
TOTAL NON-SCCP EMISSIONS	12,400.0
TOTAL SULFURIC ACID MIST EMISSIONS	351,000.0

Source: Surprenant, et al, 1976(56.).

TABLE 3-5. 1974 NATIONAL EMISSIONS OF VINYL CHLORIDE

Source Category	Vinyl Chloride (1000 kg/yr)
SCCP Sources	NA[a]
Non-SCCP Sources	
Industrial Processes	
Polyvinyl Chloride	78,639.6
Vinyl Chloride - Ethylene Dichloride	10,357.0
Vinyl Chloride - Acetylene	530.7
Caprolactam	155.1
1,1,1 - Trichloroethane	135.2
Polyvinylvinylidene Chloride	61.9
Ethylene Dichloride - Oxyhydrochlorination	0.0
TOTAL VINYL CHLORIDE EMISSIONS	89,900.0

[a] NA means no information available.

Data Source: Eimutis, et al, 1978(66.).

TABLE 3-6. 1974 NATIONAL EMISSIONS OF TOTAL REDUCED SULFUR AND REDUCED SULFUR COMPOUNDS (1000 kg/yr)

Source Category	Hydrogen Sulfide	Dimethyl Sulfide	Dimethyl Disulfide	Carbon Disulfide	Carbonyl Sulfide	Mercaptans
SCCP Sources	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]
Non-SCCP Sources						
Industrial Process						
Carbon Black-Furnace	44,617.9			44,617.9	14,872.6	
Natural Gas Processing	8,572.4					
Petroleum Refining - Sulfur Plant	57,624.4			8,550.7	8,550.7	
Petroleum Refining - Vacuum Distillation	8,515.2					
Wood Processing - Neutral Sulfite Semichemical	4,122.6					
Rayon - Semisynthetic Viscose Rayon	1,327.6			1,217.0		
Sodium Hydrosulfide - Sodium Bisulfide or Sulfhydrate	22.9					
Fish & Seafood Canning	20.4					
Methyl Mercaptan	4.5					
Wood Processing - Kraft or Sulfate Process	179,544.3					74,131.0
Wood Processing - Neutral Sulfite Semichemical						1,470.1
Captafal				0.7		
Falpet				0.7		
Mixed Olefinic Product	71.2					
Carbon Tetrachloride - Chlorination of Propane				589.7		
Carbon Tetrachloride - Carbon Disulfide				531.6		
Coffee Roasting		114.0	534.2	36.0		
Phosphoric Acid - Thermal Process	53.5					
Captan				4.5		
TOTAL EMISSIONS	304,000.0	144.0	534.0	55,500.0	23,400.0	75,600.0

[a] NA means no information available.

Pollutant

Hydrogen sulfide
Mercaptans
Carbon disulfide
Carbonyl sulfide
Dimethyl disulfide
Dimentyl sulfide

Hydrogen sulfide emissions comprise over half of all total reduced sulfur and reduced sulfur compound emissions from non-SCCP sources. It should be noted that, since available data sources did not provide emissions information on methyl mercaptans separately, emissions of all mercaptans are shown on the table. Of the industrial processes, Carbon Black-Furnace, Petroleum Refining-Sulfur Plant and Wood Processing - Kraft of Sulfate Processes produce the largest quantity of these pollutants.

3.6 SUMMARY OF EMISSIONS

Table 3-7 summarizes the total emissions for SCCP and non-SCCP sources for the twelve pollutants. Of the trace elements, SCCP sources produce nearly all of the beryllium and about 65 percent of the fluoride emissions nationally. Non-SCCP sources generate about 75 percent of the mercury emissions. Asbestos, vinyl chloride, and all total reduced sulfur and reduced sulfur compounds are emitted exclusively by non-SCCP sources, according to available data. Sulfuric acid mist is produced primarily by SCCP sources.

Conclusions on this emissions inventory are based on information found in available data sources. All tables except that for sulfuric acid mist are based on data from Reference 66, Eimutis, et al, (1978). According to one of the authors of the document, information presented in this source was based on 1974 NEDS data. Some of these data were updated when new information became available. Other sources indicated that *de minimis* pollutant information had not been updated beyond 1974. Also, this document is not all inclusive or exhaustive. Data are more complete for some pollutants than others. If data were not included for certain source categories, this may be due either to a lack of information on the source,

TABLE 3-7. COMPARISON OF SCCP VERSUS NON-SCCP POLLUTANT EMISSIONS (1000 kg/yr)

Pollutant	Total SCCP Emissions	Total Non-SCCP Emissions
Mercury	51.2	150
Beryllium	266	0.3
Asbestos		657
Fluorides	32,600	17,300
Sulfuric Acid Mist	339,000	12,400
Vinyl Chloride		89,900
Total Reduced Sulfur		
Hydrogen Sulfide		304,000
Mercaptans		75,600
Dimethyl Sulfide		114
Dimethyl Disulfide		534
Reduced Sulfur Compounds		
Hydrogen Sulfide		see above
Carbon Disulfide		5,500
Carbonyl Sulfide		23,400

or that a certain pollutant may not be emitted from this source. Also, in rounding, certain values may be reduced to 0.0, but this is not necessarily an indication that a pollutant is not being emitted from a source.

Information on sulfuric acid emissions was derived from two sources. Non-SCCP data were obtained from Reference 66, Eimutis, et al, (1978). Sulfuric acid emissions from SCCP sources were estimated by applying the emission factors in Table 4-6 to a nationwide inventory of sulfur oxides (reported as SO_2) from Reference 56, Surprenant, et al, (1976). This document was based on a survey of data existing in literature and information supplied through contact with industry, government and academic laboratories.

4. EMISSION FACTORS

This chapter presents pollutant emission factors for stationary conventional combustion processes (SCCP). The factors are summarized from the CCEA information base and are primarily a result of extensive data surveys being conducted under EPA's Emissions Assessment of Conventional Combustion Systems (EACCS) program. A discussion of the development of these factors is presented in Section 5. Section 6 contains a discussion of the variability of actual emission factors and the expected uncertainty in emission values calculated with the mean factors presented here.

4.1 TRACE ELEMENTS

Tables 4-1 through 4-5 summarize trace element emission factors for the predominant combustion source categories. The trace elements subject to the de minimis guidelines are mercury, beryllium, and fluorides. Because the trace element emission factor data base was relatively undeveloped for industrial and commercial/institutional combustion processes, emission factors for these combustion sources were based on similarities to other combustion sources for which a more extensive data base was developed. Accordingly, Tables 4-1 to 4-3 present equivalent trace element emission factors for utility and industrial boilers, with the values of the factors being based primarily on the more extensive emissions data base available for utility boilers. Values of emission factors for commercial/institutional combustion sources (Table 4-5) are also based primarily on the data base for utility boilers. The rationale for the use of utility boiler data for industrial and commercial/institutional emission factors is discussed in Section 5.

All emission factors are presented in terms of weight of the pollutant per unit heat input of fuel. In addition, most emission factors are presented in terms of the concentration of the pollutant in the fuel. Thus, source specific emission factors may be determined if fuel composition and fuel feed rate are known. For the case of utility (or industrial) coal-fired boilers, a parameterized factor (see Table 4-1) is available to characterize source specific beryllium emission factors when values of influence parameters (i.e., enrichment ratio, particulate control efficiency) are known.

TABLE 4-1. TRACE ELEMENT EMISSION FACTORS FOR CONTROLLED COAL-FIRED UTILITY AND INDUSTRIAL BOILERS

FURNACE TYPE	CONTROL DEVICE	BITUMINOUS COAL pg/J			LIGNITE COAL pg/J		
		Hg	Be	F	Hg	Be	F
Pulverized Dry Bottom	Electrostatic Precipitator	39C	2.3C	40C	64C	0.7C	50C
Pulverized Dry Bottom	Mechanical Precipitator	39C	7.8C	40C	64C	19C	50C
Pulverized Dry Bottom	Wet Scrubber	7.8C	0.2C	8.0C	13C	0.3C	10C
Pulverized Wet Bottom	Electrostatic Precipitator	39C	1.9C	40C	64C	-	50C
Pulverized Wet Bottom	Mechanical Precipitator	39C	6.3C	40C	64C	-	50C
Pulverized Wet Bottom	Wet Scrubber	7.8C	0.2C	8.0C	13C	-	10C
Cyclone Boiler	Electrostatic Precipitator	39C	0.4C	40C	64C	0.4C	50C
Cyclone Boiler	Mechanical Precipitator	39C	1.3C	40C	64C	18C	50C
Cyclone Boiler	Wet Scrubber	7.8C	0.03C	8.0C	13C	0.2C	10C
Stoker	Baghouse	2.0	0.06	10	-	-	-
Stoker	Mechanical Precipitator	6.2	5.5	3540	2.4	5.9	423
Stoker	Wet Scrubber	-	-	-	-	-	-
Stoker	Electrostatic Precipitator	-	-	-	0.23	0.11	638

General Notes:

1. For Be, the emission factor may be computed from the general equation $E=\frac{C}{H}\cdot f\ (1-E)ERX10^3$(see Section 5.1.1) when source specific values of the variables are known.
2. Most emission factors are shown in terms of C, the trace element content in the coal. C is in units of µg/g, or ppm. Typical values of C for bituminous coal are 0.2, 0.9 and 100 for Hq, Be, and F, respectively. Typical values for lignite are 0.16, 0.8 and 37 for Hg, Be, and F, respectively. The limited data base for stoker units did not permit the expression of emission rates in terms of C.
3. Blanks in the table indicate that no emission factor is reported in the existing data base. The source configurations corresponding to these blanks are rarely encountered at industrial or utility boiler installations.
4. Emission factors presented in this table are based on reference 1, (Shih,et al, October 1979) and reference 56 (Surprenant, 1976).
5. Emissions for anthracite coal are not reported in the existing data base. However, the amount of anthracite coal used by combustion processes is very small (see Table 4-7) and expected to decrease to still lower levels of consumption in the future.
6. To convert emission factor units to $LB/10^{12}BTU$, multiply factors by 2.33.

TABLE 4-2 TRACE ELEMENT EMISSION FACTORS FOR UNCONTROLLED COAL-FIRED UTILITY AND INDUSTRIAL BOILERS

FURNACE TYPE	BITUMINOUS COAL pg/J			LIGNITE COAL pg/J		
	Hg	Be	F	Hg	Be	F
Pulverized dry bottom	39C	26C	40C	64C	81C	50C
Pulverized wet bottom	39C	21C	40C	64C	--	50C
Cyclone boiler	39C	4.4C	40C	64C	67C	50C
Stoker	6.2	18	3540	2.4	24	423

General Notes:

1. Emission factors presented in this table are based on Reference 1 (Shih, et al 1979).
2. Most emission factors are shown in terms of C, the trace element content (in μg/g or ppm) in the coal. The limited data base for stoker units did not permit the expression of emission rates in terms of C.
3. Blanks indicate that no emission factor is reported in the existing data base.
4. To convert emission factor units to LB/10^{12}BTU, multiply factors by 2.33.

TABLE 4-3 TRACE ELEMENT EMISSION FACTORS FOR OIL-FIRED AND GAS-FIRED UTILITY AND INDUSTRIAL BOILERS

FURNACE TYPE	RESIDUAL OIL[a] pg/J			NATURAL GAS[b] pg/J		
	Hg	Be	F	Hg	Be	F
UNCONTROLLED[c]						
Tangential firing	23C	24C	23C	4.9	Nil	Nil
Wall firing	23C	24C	23C	4.9	Nil	Nil

(a) Emission factors for residual oil are calculated based on characterization of eleven residual oil samples and the assumption that all trace elements in the oil feed are emitted through the stack (Shih, et al, October 1979). C indicates the concentration of trace element in residual oil, in ppm.

(b) Based on stack test measurements for gas-fired utility boilers (1.).

(c) When boilers are equipped with wet scrubbers (used for flue gas desulfurization), the emission factor for Be may be assumed to be 0.01 times the uncontrolled factor given above, and emissions of Hg and F are .2 times the values given above (1.).

NOTE: To convert emission factor units to LB/10^{12}BTU, multiply factors by 2.33.

TABLE 4-4. TRACE ELEMENT EMISSION FACTORS FOR INTERNAL COMBUSTION SOURCES

SOURCE TYPE	DISTILLATE OIL			NATURAL GAS		
		pg/J			pg/J	
	Hg	Be	F	Hg	Be	F
Gas turbine	.39	.14	--	4.9	Nil	Nil
Reciprocating engine	.13	.03	--	4.9	Nil	Nil

General Notes:

1. Emission factors are based on characterization of fuel samples as described in Reference 57 (Shih et al, February 1979) with the exception of emissions for Hg from natural gas-firing which are based on stack test measurements for gas-fired utility boilers as reported in Reference 1 (Shih, et al, October 1979).
2. Blanks in the table indicate that no emission are reported in the existing data base.
3. To convert emission factor units to LB/10^{12}BTU, multiply factors by 2.33.

TABLE 4-5. TRACE ELEMENT EMISSION FACTORS FOR UNCONTROLLED COMMERCIAL/ INSTITUTIONAL EXTERNAL COMBUSTION

TYPE OF FURNACE	EMISSION FACTOR , pg/J		
	Hg	Be	F
Bituminous Coal:			
Pulverized Dry Bottom	39C	26C	40C
Pulverized Wet Bottom	39C	21C	40C
Stoker	6.2	0.6C[b]	3540
Residual Oil			
Tangential or Wall firing	23C	24C	23C
Natural Gas			
Tangential or Wall firing	4.9	Nil	Nil

(a) Unless otherwise noted, emission factors above are based on reference 1 (Shih, et al, October, 1979).

(b) The emission rate of Be from Stokers was determined by adjusting the emissions factor for utility stokers. The adjustment was made by comparing the coal ash/fly ash ratio for utility boilers versus the coal ash/fly ash ratio for commercial/institutional boilers. (See discussion of Section 5.1.4.)

(c) The term C in the emissions factor indicates the concentration of trace element in the fuel, in ppm.

NOTE: To convert emission factor units to LB/10^{12}BTU, multiply factor by 2.33.

Tables 4-1 through 4-5 present emission factors for the trace elements mercury, beryllium, and fluorides. Depending on the type of emission control, fuel, and fuel composition, it is possible that emissions from some new utility or industrial boilers would exceed the proposed _de minimis_ emission rates for these pollutants. For example, a 500 MW pulverized dry bottom boiler (operating at 60 percent capacity and 40 percent overall efficiency) burning typical bituminous coal and controlled to meet the New Source Performance Standards (NSPS) for criteria pollutants would be expected to emit about 0.004 metric tons per year of beryllium, 0.04 metric tons per year of mercury and 10 metric tons per year of fluorides. These emission levels are nearly equivalent to the proposed _de minimis_ levels of 0.004 and 0.2 metric tons per year for beryllium and mercury, and greater than the proposed level of 0.02 metric tons per year for fluorides. When coal of high trace element composition is used, the _de minimis_ levels may also be exceeded for mercury and beryllium. However, for NSPS controlled coal-fired boilers of average size (100 to 500 MW), the trace element _de minimis_ levels would normally be exceeded only for fluorides. These calculated emission values are subject to some uncertainty because of variabilities in the parameters used for the calculation, especially for beryllium emissions from coal combustion. These uncertainties are discussed in Section 6.

Emissions from large oil fired boilers burning low sulfur fuel and not equipped with flue gas desulfurization (FGD) units would be expected to exceed the _de minimis_ levels for beryllium and fluorides. For example, a 500 MW oil fired boiler (operating at 60 percent capacity and 40 percent overall efficiency) would emit 0.05 metric tons per year of beryllium and 0.06 metric tons per year of fluorides (assuming a typical fuel composition of 0.08 and 0.12 ppm for Be and F, respectively). These emission levels exceed the _de minimis_ levels of 0.004 and 0.02 metric tons per year for beryllium and fluorides. Respectively, however, when the same boiler is equipped with an FGD unit to achieve the NSPS, the expected emission levels would be 0.005 and 0.013 metric tons per year for beryllium and fluorides, respectively.

It should be noted that the relatively high stacks (e.g., 100 to 200 M) associated with large boilers would probably preclude the possibility that emissions from these sources would result in levels exceeding the de minimis ambient air guidelines, despite the expectancy that the de minimis emission levels may be exceeded in some cases.

4.2 SULFURIC ACID MIST

Table 4-6 summarizes sulfuric acid emission factors for various uncontrolled combustion sources. Because the data base was limited, emission factors were combined into the overall source categories shown. While insufficient data exist to quantify the influence parameters affecting H_2SO_4 emissions, it should be noted that the values in Table 4-6 may change significantly depending on oxygen levels in the flue gases, power level of the process, and the concentration of trace elements vanadium, magnesium, and sodium in the fuel.

Sulfuric acid emission levels from large coal and oil fired external combustion sources would be expected to exceed the de minimis level of one metric ton per year. When a wet scrubber is used to meet the NSPS, the expected emissions of sulfuric acid mist from a 500 MW boiler (operating at 60 percent capacity and 40 percent overall efficiency) burning bituminous coal of two percent sulfur would be 210 metric tons per year. The expected emissions of sulfuric acid mist from a 500 MW boiler controlled by wet scrubbing and burning two percent oil would be 420 metric tons per year.

Emissions of sulfuric acid mist from internal combustion units are not likely to exceed the de minimis levels. The average size of these sources is about 2 MW, and sulfuric acid emissions are not expected to be greater than about one metric ton/year per unit (reciprocating engine or gas turbine).

TABLE 4-6. EMISSION FACTORS FOR SULFURIC ACID MIST FROM COMBUSTION SOURCES

SOURCE	Percent of fuel Sulfur in H_2SO_4	Emission Factor[a] ng/J	Information Sources (Reference no.)
UNCONTROLLED [b]			
EXTERNAL COMBUSTION			
Bituminous coal-fired utility boilers	.74	8.8S	58,22,2,14,56
Oil-fired utility boilers	2.4	16.9S	59,58,56
INTERNAL COMBUSTION			
Distillate oil-fueled gas turbine	3.8	1.5	60,61
Distillate oil-fueled reciprocating engine	1.4	8.9S	62,57
Gas-fueled internal combustion	Nil	Nil	57

(a) Some emission factors are presented in terms of S, the percent sulfur in the fuel. The limited data base for distillate oil-fueled gas turbines did not permit the expression of emission rates in terms of fuel sulfur concentration.

(b) For controlled emission rates, multiply uncontrolled levels above by 0.50 when flue gas desulfurization units are used, 1.0 when cold side ESPs or mechanical precipitators are used, and 2.4 when hot side ESPs are used (63, 64, 65, 67, 68),

NOTE: To convert emission factor units to LB/10^{12}BTU, multiply factor by 2.33.

4.3 ASBESTOS AND VINYL CHLORIDE

An information search revealed no available emission data for asbestos or vinyl chloride from stationary combustion sources. Potential emission sources of asbestos from combustion systems were identified as internal insulation materials, coal, and limestone used in flue gas desulfurization units. Emissions of asbestos from any of these sources is expected to be negligible. More data are needed to accurately quantify the significance of the potential sources. Potential emissions of vinyl chloride are not expected to exceed the de minimis emission levels. Conditions in the combustion environment are extremely unfavorable for the information of vinyl chloride, and existing emission data for hydrocarbon emissions indicate low emissions levels for hydrocarbon groups containing vinyl chloride. Specific emission data for vinyl chloride are needed to accurately quantify an emission factor for this compound.

5. DEVELOPMENT OF EMISSION FACTORS

The estimation of environmental loadings arising from combustion processes depends on characterization of the emission rates peculiar to the various combustion sources. The characterization of emissions of noncriteria pollutants such as those considered for de minimis cutoff levels is a special problem because the data base is often inadequate. This chapter discusses the manner in which the available data base has been used to develop the pollutant emission factors presented in Section 4. for stationary conventional combustion sources.

5.1 TRACE ELEMENT EMISSIONS

Trace elements which are considered for de minimis cutoffs are mercury, beryllium, and fluorides. Mercury and fluorides are discharged to the atmosphere primarily in the gas phase, and it is plausible to assume that all quantities present in the coal feed are emitted to the stack. The emission rate of beryllium, on the other hand, depends on the partitioning of the element between particles in the flyash and bottom ash fraction, and between flyash particles in the control device collector and the control device exhaust.

5.1.1 External Combustion - Utility Boilers

Trace element emission rates depend greatly on the type of fuel. Three principal fuels are used: coal, residual oil, and natural gas.

Coal Combustion

The existing data base for trace element emissions from coal fired utility boilers is discussed extensively in Volume III of the Emissions Assessment of Conventional Combustion Sources (1.). The data base was developed from a large number of reference sources, as listed at the conclusion of this report. The major drawbacks in the data base concern the limited information with respect to trace element emissions from lignite combustion and the absence of data for trace element emissions from stoker units. Also, the data base contained limited information for the characterization of trace element emissions from sources controlled by mechanical precipitators and wet scrubbers.

Because trace element emissions are dependent on a number of factors, including trace element content of coal, boiler firing configuration, boiler size, and particulate control device efficiency, it is practical to develop trace emission factors in a parameterized format to account for the effect of the more important variables. In the EACCS program (1.), the equation used to calculate trace element emission factors is:

$$EF = \frac{C}{H} \cdot F\ (I-E)\ ER \times 10^3$$

where EF = emission factor for a specific trace element, ng/J

C = concentration of element in coal, μg/g

H = higher heating value of coal, kJ/kg

F = fraction of coal ash as fly ash

E = fractional particulate collection efficiency of control device.

ER = enrichment factor for the trace element (ratio of concentration of element in emitted flyash to concentration of element in coal ash)

The use of enrichment factors enables direct comparison and compilation of trace element emission data on a normalized basis. This normalization scheme is appropriate because the enrichment behavior of trace elements is generally consistent, despite differences in furnace or coal types, and sampling or analysis procedures (1. through 13.).

Unique emission rates are associated with different sets of fuel type, boiler type and control device type. Table 4-1 in Section 4. summarizes the emission factors for these sets, as computed in the EACCS program using the available data base and the equation above.

TABLE 5-1. EFFICIENCIES OF CONTROL SYSTEMS

	Bituminous Coal	Lignite Coal	
	All Boilers	Pul. Dry Bottom	Cyclone
Electrostatic precipitator	.98	.99	.99
Mechanical precipitator	.70	.76	.73
Wet Scrubber	.99	.99	.99

Note: Based on data base comprised of References 3., 4., 14. through 22.

TABLE 5-2. FRACTION OF COAL ASH AS FLY ASH IN COAL FIRING

	Bituminous Coal	Lignite Coal
Pulverized dry bottom	.80	.35
Pulverized wet bottom	.65	---
Cyclone	.135	.30
Stoker	.60	---

Note: Based on evaluations conducted in the EACCS program (1.), using data base comprised of References 3., 4., 14. through 22.

Enrichment factors used to calculate trace element emission factors were determined in the EACCS program by averaging values reported by the various reference sources of the existing data base. Since enrichment factors depend on the efficiency of the emission control device, separate factors were determined for three types of control devices; electrostatic precipitators, mechanical precipitators, and wet scrubbers.

Based on evaluations conducted in the EACCS program (1.), the fractional collection efficiencies for coal-fired boilers are shown in Table 5-1. These efficiencies represent the average control observed for installations associated with the trace element emissions data base. The control levels for electrostatic precipitators and wet scrubbers are sufficient to attain compliance with the New Source Performance Standards for boilers.

The average fraction of coal ash produced as fly ash varies with coal type and boiler type as shown in Table 5-2.

Concentrations of trace elements for bituminous coal and lignite were tabulated from published U.S. Geological Survey Data (24.) and the computerized National Coal Resources Data System (23.), and supplemented by other reference sources (25. through 54.). The average values for trace element concentrations were determined by weighting the area specific concentrations with annual production by county (55.).

The calculation of emission factors for mercury and fluorides does not require the calculation of enrichment factors, since these elements are discharged from coal combustion primarily in the gas phase. If mechanical or electrostatic precipitators are used to control emissions, it is assumed that all amounts of these elements contained in the coal are emitted through the stack. When wet scrubbers are used, the data base indicates an average removal efficiency of eightly percent for mercury and fluorides (1.).

The data base compiled in the EACCS program contained no information for trace element emissions from stoker units. Consequently, a test program was conducted as a part of the EACCS program to obtain the necessary data. Because the data resulting from these tests are limited, and because trace element analyses were performed using semiquantitative analysis techniques, enrichment factors were not calculated from the data, and it is not possible to normalize the test results with respect to trace element composition in the fuel. Hence, for the limited stoker units tested, the differences in trace element contents of the various fuels and control devices result in substantial variation in the test results and the calculated emission factors.

Trace element emission factors for uncontrolled utility boilers were estimated by factoring out the effects of control devices from the extensive data base compiled for controlled boilers. Control devices affect both the enrichment factors and overall particulate collection rates. Enrichment factors for uncontrolled boiler emissions were assumed to be equivalent to those observed for boilers equipped with the low-efficiency mechanical precipitators. The effect of the mechanical precipitator on collection of particulate matter (including trace elements) was factored out of the controlled emissions data base by applying the average collection efficiencies presented previously in this section to the emission factors of Table 4-1. The results are shown in Table 4-2. (See Section 4.1.)

Gas and Oil-Fired Boilers

The data base compiled in the CCEA program includes analysis results of residual oil samples from eleven separate oil-fired boiler sites. These trace element concentrations were used to calculate mean emission factors, assuming that all trace elements present in the oil feed are emitted through the stack (1.). The emission factors are expressed in terms of the trace element concentration in the residual oil (Table 4-3). (See Section 4.1.)

The data base for trace element emissions from gas-fired utility boilers is extremely limited. Measurements of trace element emissions from seven separate gas-fired boilers were conducted as part of the EACCS program to supplement the existing data base. However, measurements were conducted for a limited number of trace elements, and concentrations for only one of the pollutants of concern in this study, mercury, were determined.

5.1.2 External Combustion - Industrial Boilers

Emissions from industrial boilers are governed by the same principles that apply to utility boilers. However, differences in combustion equipment design and operating practices may result in differences in emission factors. Generally industrial combustion equipment is smaller and less efficiently operated than electric utility equipment, resulting in greater emission rates from industrial boilers.

GCA is currently evaluating emission rates from industrial boilers under the ongoing EACCS program. The evaluation includes a comprehensive survey of the existing data base for trace element emissions, and the calculation of trace element emission factors for various sets of boiler design, fuel type, and control device. However, the results of this effort will not be available until mid-1980. In the interim, the most comprehensive synthesis of trace element emissions data and computation of trace element emissions factors for industrial boilers is found in GCA's Preliminary Emissions Assessment of Conventional Stationary Combustion Systems (56.).

GCA estimates trace element emissions from coal-fired industrial boilers based on fuel composition and distribution of fly ash to bottom ash for the various external combustion categories. Because the data base was too limited to permit characterization of trace element enrichment behavior in the fly ash, it was assumed in this reference that trace element concentration was equally partitioned (no enrichment) between the fly ash and bottom ash. GCA then applied the fraction of coal emitted as fly ash to the trace element composition to calculate uncontrolled emission factors. Controlled emission factors were determined by adjusting the uncontrolled factors using typical particulate control efficiencies and assuming that trace elements are partitioned equally (per unit mass) between the collected matter and the matter escaping through the stack. However, since the existing data base is inadequate to characterize differences in fuel composition and fly ash/bottom ash ratios between the Industrial and Utility sectors, it is also not possible to establish separate uncontrolled emission factors for these two sectors. Similarly, since emission control capability is equivalent for both utility and industrial boilers, the controlled emission factors are the same for each of these two combustion sectors.

Since there are insufficient data (based on available data base surveys) to permit discrimination between trace element emissions from utility boilers and industrial boilers, emission factors were assigned to industrial boilers based on the recent investigation of utility boiler emissions conducted under the EACCS program (1.). This work assembled an extensive data base which permitted characterization of trace element enrichment factors, fly ash/bottom ash ratios, fuel composition, and control device efficiencies. (See Section 1.1.1.) Table 4-1 summarizes trace element emission factors for coal-fired industrial boilers. (See Section 4.1.)

The available data base for trace element emissions from oil-fired and gas-fired industrial boilers is also insufficient to permit a quantifying distinction between the utility and industrial combustion sector. Therefore, trace element emission factors for industrial boilers were assigned values equivalent to those compiled for utility boilers in the EACCS program (1.). Table 4-3 summarizes trace element emission factors for oil and gas fired industrial boilers.

5.1.3 Internal Combustion - Industrial or Electricity Generation

The data base for trace element emissions from internal combustion sources is discussed extensively in Volume II of the Emissions Assessment of Conventional Stationary Combustion Systems (57.). The data base was developed from various references and supplemented by additional test data acquired in the EACCS program.

Measurements of trace elements emissions in the stack gases from a gas fueled turbine revealed the presence of negligible or nondiscernible amounts for most of the trace elements. However, emission of mercury vapors during gas firing were of the same magnitude as those resulting during oil-firing and are consistent with the levels observed in tests of utility boilers (as discussed earlier in Section 5.1.1). Table 4-4 shows trace element emission factors for gas-fired turbines.

Table 4-4 also presents trace element emissions data for distillate oil-fueled gas turbines and distillate oil (diesel fuel) engines. The emissions data were based on the trace element content of the fuel used at various test facilities, and represent maximum potential emission rates. The emission factors for the turbine and engine are of the same order of magnitude, and are the result of the similarity between the trace element content of turbine and engine fuels.

5.1.4 External Combustion - Commercial/Institutional

GCA is currently evaluating emissions from commercial/institutional combustion systems under the ongoing EACCS program. The evaluation will include a comprehensive survey of the existing data base for trace element emission, and the determination of trace element emission factors for various sets of boiler design and fuel type. Until the results of this effort are available, the most comprehensive synthesis of trace element emissions data for commercial/institutional combustion systems is found in GCA's Preliminary Emissions Assessment of Conventional Stationary Combustion Systems (56.). In this document, GCA estimates trace element emissions factors from commercial/institutional combustion systems for coal-fired boilers based on fuel composition ratio of fly ash to bottom ash for the various combustion categories. Trace element concentration is assumed to be equally partitioned between bottom ash and fly ash. The fly ash/bottom ash ratio is assumed to be the same as that for industrial boilers, with the exception of stoker units. For stoker units, the fly ash/bottom ash ratio is assumed to be 5/95 as compared to 35/65 for industrial stokers. Hence, emission factors for trace elements from commercial/institutional stoker units are seven times less than from industrial stoker units. This relative difference was applied to stoker emission factors for the industrial sector to calculate emission factors for commercial/institutional stoker units. The emission rate for other combustor types is assumed to be the same as that for industrial boilers. The emission factors are shown in Table 4-5. (See Section 4.1.)

The available data base for trace element emissions from oil-fired and gas-fired commercial/institutional boilers is insufficient to permit a quantifying distinction between the various boiler sectors. Therefore, trace element emission factors for commercial/institutional boilers were assigned values equivalent to those compiled for utility boilers in the EACCS program (1.). Table 4-5 summarizes trace element emission factors for oil and gas fired commercial/institutional boilers.

5.2 ASBESTOS EMISSIONS

Asbestos is the generic term for any of six naturally occurring crystalline mineral hydrated silicates. Asbestos occurs in a fibrous state, and is formed by the metamorphosis of serpentine and amphibole minerals.

Asbestos emissions result from the mining of asbestos ores, the milling of asbestos ores for production of five fibrous asbestos materials, and the manufacture and end use of various asbestos-containing materials. Based on existing emission inventories, it is estimated that 90 percent of asbestos emissions arise during mining, manufacturing or production of asbestos, while it is estimated that five percent of the total asbestos emissions result from end-uses of asbestos-containing products (69.).

No accurate asbestos emission factors are reported in the existing data base. Existing emission inventories developed for asbestos are based on engineering judgments and very limited data. The CCEA information base was searched for data on asbestos emissions from stationary combustion systems, fuel and fly ash composition studies were evaluated, emission inventories for noncriteria pollutants were examined, and various cognizant individuals of pertinent agencies were consulted.

One possible source of emissions resulting from end-use of asbestos in combustion systems is internal insulation in boiler breechings and ducts. The rate of erosion of internal asbestos insulation is unknown, and the integrity of the eroded fibers as an asbestos form is not known. However, it is not expected that the quantity of emitted insulation materials would approach the de minimis emission levels. For example, if asbestos emissions resulted only from insulation loss, a stack emission rate of one ton per year of asbestos (the de minimis level) would be equivalent to the loss of approximately 90 tons per year of asbestos insulation from the boiler equipment, assuming the stack emissions are controlled for particulate matter. As this depletion rate is several orders of magnitude greater than the amount of internal insulation used in a large boiler installation, it is apparent that emissions of eroded insulation are actually negligible.

Moreover, the use of asbestos insulation is no longer commonplace, as other insulating materials with greater resistance to high temperatures are presently being used instead. Use of these substitute insulation materials also avoids the hazards previously experienced from exposure to asbestos emissions during application of the insulator to the boiler equipment.

Other potential sources of asbestos emissions are flue gas desulfurization (FGD) units which use limestone as the scrubbing medium. In some deposits, limestone is known to contain the asbestos fibers tremolite and actinolite (72.). As combustion flue gases are treated in a limestone FGD unit, trace amounts of asbestos may be generated and emitted out the stack. No information is available from the existing data base to characterize the chemistry associated with asbestos emissions from limestone scrubbers or the quantities of asbestos which may arise.

Still another potential asbestos emission source in combustion systems is coal itself. However, only trace amounts of minerals are usually found in coal deposits and it is not expected that detectable amounts of asbestos occur in coal (71.). Moreover, it is expected that the normal temperatures produced in the combustion zone are sufficient to disintegrate any asbestos fibers present (70.).

In the development of the present national emission standards for asbestos, various mining, processing, manufacturing and end-use sources of asbestos emissions were considered. However, stationary combustion systems were not addressed as a source of concern. Preliminary investigations should be conducted to assess the significance of asbestos emissions arising from potential sources in combustion systems.

5.3 SULFURIC ACID MIST EMISSIONS

Sulfuric acid (H_2SO_4) is a product found in the flue gases of combustion systems. It is formed when SO_2 in the combustion gases in oxidized to SO_3, followed by the combination of SO_3 with water vapor in the stack gas. Sufficient water vapor exists in the stack to convert essentially all SO_3 to H_2SO_4 before it is finally emitted out the stack. As the H_2SO_4 is emitted and is cooled to temperatures below the acid dew point, it is transformed to a liquid aerosol known as "sulfuric acid mist".

Sulfuric acid may be adsorbed on solid particulate matter in the stack or condensed on boiler surfaces. This results in the formation of metal surfates (MSO_4) and corrosion products. The sulfates which are formed, the SO_3, and the H_2SO_4 vapor and liquid aerosol, are all referred to as primary sulfates. (Secondary sulfates are sulfur oxidation products formed in the atmosphere.)

Because current analytical methods and reporting procedures for primary sulfates vary, the resulting emissions data may be misleading. Generally, the analytical approaches used allow a separate determination of particulate and gaseous forms of the primary sulfates (64.). The gaseous sulfates, consisting of H_2SO_4 and SO_3, are collected by filter for analysis by wet chemical techniques. Depending on the temperature of the filter and the sampled stack gases, some fraction of the H_2SO_4 present in the sample stream will be collected by the filter as aerosol particulate matter. The aerosol H_2SO_4 on the filter is indistinguishable from the particulate sulfates during analysis, and is included as total particulate sulfate. In sampling systems using high temperature probes and filters, the portion of H_2SO_4 collected by the particulate filter is minor, while systems which sample isokinetically from the stack may contain significant portions of aerosol H_2SO_4 which is collected on the filter (78.). Thus, emissions data surveys for average emission levels tend to understate the actual level of H_2SO_4 to some degree, depending on the type of sampling procedures associated with the data base. However, this understatement is mitigated to some degree, considering that some H_2SO_4 is adsorbed on particulate matter between the stack sample point (typically near the base of stack) and the stack exit.

Emissions of SO_3 and H_2SO_4 depend on numerous operating parameters. The parameter causing the most pronounced effect on SO_3/H_2SO_4 emissions is the amount of excess oxygen supplied to the burners. Low excess air operation is most practical in oil-fired systems, whereas the technology for burning pulverized coal at low oxygen levels is not available. Excess air must be less than two percent to decrease SO_3 formation by one half from normal operation at twelve to 20 percent excess air. SO_3 concentration can be reduced to essentially zero at 0.1 percent oxygen in the flue gas (63.).

Sulfuric acid concentration in flue gas is also related to the boiler load factor (i.e., the operating power level compared to the design full power level), the sulfur content of the fuel, and the concentrations of vanadium, magnesium, and sodium in the fuel. The latter trace elements introduce a catalytic effect on the reaction of SO_2 to SO_3. Recently, studies have been conducted to quantify the relationship of the various influence factors affecting sulfuric acid and sulfate emissions (67.). Such models are in formative stages of development, and may be useful when plant specific data are available to characterize the influence variables and calibrate the model.

Emissions data for H_2SO_4 (including SO_3 reported as H_2SO_4) are presented in Table 4-6. Because the data were very limited for some boiler firing types, data were combined into the general source categories shown. However, the variability of the combined emissions data base is less than 0.7, and may, under the criteria established in the EACCS program (1.), be considered an adequate portrayal of SO_3/H_2SO_4 emissions from utility boilers. No data for lignite-fired utility boilers were found.

In the absence of emissions data for industrial boilers, the emission rate of SO_3/H_2SO_4 from industrial boilers was assumed to be equivalent to that of utility boilers.

The most extensive survey of the SO_3/H_2SO_4 emissions data base for internal combustion sources was developed in the EACCS program (57.). The SO_3/H_2SO_4 emission data base was found to be adequate for oil fueled gas turbines; however, limited data were available to characterize SO_3/H_2SO_4 emissions from reciprocating engines. Table 4-6 summarizes the emission factors and information sources for internal combustion sources.

Conventional control equipment which is used to reduce emissions of particulate matter and SO_2 from flue gases may also affect emissions of sulfuric acid. Of the controls used, flue gas desulfurization systems exert the greatest impact on H_2SO_4 emissions. Evaluation of data for lime and limestone scrubbers at various coal-fired sources (63.) has shown that desulfurization systems operating at 80 to 90 percent SO_2 removal also removal about 50 percent of the SO_3 and H_2SO_4 in the flue gas. Evaluation of test data for emissions from conventional electrostatic precipitator (ESP) installations at coal and oil-fired sites has shown that an ESP has no effect on the concentration fo SO_3/H_2SO_4 in the flue gases (64.). However, emissions of SO_3/H_2SO_4 may increase appreciably when an ESP is installed upstream of heat recovery equipment ("hot side" configuration).. Electrical arcing across the ESP electrodes converts SO_2 to SO_3 rapidly at the higher temperatures in the hot side ESP (65.). In limited tests conducted at a coal-fired industrial boiler equipped with a hot side ESP, flue gas concentrations of SO_3/H_2SO_4 increased by 242 percent through the ESP (65.).

5.4 VINYL CHLORIDE EMISSIONS

No emissions data for vinyl chloride were reported in the CCEA data base. Some specific organic compounds have been identified in flue gases of combustion systems, but quantitative data on the emissions of these compounds is extremely limited. Generally, conditions of high temperature, mixing, ample residence time and excess oxygen in the combustion environment have been considered unfavorable for formation of organic compounds in quantities which could cause significant environmental concern. In fact, a common method used to control emissions of chlorinated hydrocarbons (i.e., vinyl chloride) from manufacturing facilities involves incineration in steam boilers (220). This control technique has been used in existing boilers without affecting normal operations or boiler efficiency.

Although the amount of vinyl chloride emission in flue gases cannot be determined specifically, the quantitative emissions data base does demonstrate that emission levels of vinyl chloride from combustion systems will not exceed the de minimis levels. Table 5-3 shows emissions factors for C_3 alkanes measured in stack gases for various utility boilers and fuel types in the EACCS program (1.). The data were obtained by chromatograph using a normal boiling point retention time calibration, according to EPA's Level 1 Method. As the boiling point of vinyl chloride is -13.9 C, the chromatograph will report this compound in the range of C_3 alkanes in terms of propane (74.). Thus, assuming that as much as ten percent of organics reported as C_3 alkanes are vinyl chloride (a conservative assumption, considering the stability and formation potential of vinyl chloride relative to other more common alkanes), and that the greatest expected emission rate would be 410 pg/J (see Table 5-3), the total emissions of vinyl chloride

Table 5-3. EMISSIONS OF C_3 HYDROCARBONS FROM UTILITY BOILERS

Combustion Source	Maximum Emission Rate Reported pg/J
Bituminous Coal-fired Utility Boilers	
pulverized dry bottom	320
pulverized wet bottom	160
cyclone	280
stoker	320
Lignite-fired Utility Boilers	
pulverized dry bottom	410
cyclone	260
stoker	370
Oil-fired Utility Boilers	
tangential firing	320
wall-firing	340
Gas-fired Utility Boilers	
tangential-firing	200
wall-firing	250

Source: Shih, C., et al, 1979(1.)

from a 500 MW lignite fired boiler would be 0.7 tons per year. This is less than the de minimis level of 1 ton per year.

5.5 TOTAL REDUCED SULFUR AND REDUCED SULFUR COMPOUND EMISSIONS

Theoretically, under normal combustion process conditions all of the sulfur, in any type of fuel, would be converted to sulfur oxides, most of which is sulfur dioxide. Sulfur trioxide and primary sulfates are also formed in the oxidative process. It has been observed (80.), however, that less than the expected amount of sulfur is completely oxidized. The actual amount is usually from 79 to 99 percent. The remaining sulfur may be found as sulfur compounds retained in coal and oil bottom ash or slag in the form of metal sulfides. If reduced sulfur compounds exist in a combustion (oxidation) process as a part of the flue gas, it would have to be under reducing combustor conditions. Combustion thermodynamics, which would govern the formation of any sulfides, are a function of the following parameters:

- Fuel type: percent sulfur, percent ash and concentration of metals
- Temperature and air/fuel ratio (stoichiometry)
- Mode of combustion: type of firing, time in combustor, etc.
- Kinetic limitations of the sulfur reactions

The CCEA information base was searched for data on emissions, analytical methods of determination, fuel combustion and studies, and any mass balance approaches to reduced sulfur evaluation. National emission inventories for noncriteria pollutants were examined for historical reduced sulfur emissions, and persons knowledgeable in the field were contacted.

Very little pertinent information is available. One report (80.) contains information on hydrogen sulfide, carbonyl sulfide, and carbon disulfide. This information was limited to a mole fraction computer study of sulfur distribution in four types of coal. The other (83.) included total sulfide and total reduced sulfur species as a percent of oil and coal fired fly ash composition. In either case the recorded levels are always less than 0.01 percent of the sulfur in fuel. The report states that "although the method of determination of sulfate might measure other sulfur species, determinations have shown the presence of other sulfur forms to be negligible". While examination of the literature reveals that many of these sulfur compounds have been observed at coal gasification and oil refinery sources (81.,82.), no other combustion emissions data nor any other analytical procedures are mentioned for the measurement of total reduced and reduced sulfur pollutants from conventional combustion sources.

Furthermore, all persons contacted (see Appendix A) have no knowledge of any reports or ongoing projects that measure the sulfur compounds at conventional combustion sites. Most of them informally agreed to the assumption, a priori, that one would not expect appreciable amounts of these pollutants in an oxidative process.

6. SAMPLING AND ANALYSIS PROCEDURES USED TO OBTAIN EMISSIONS DATA

This section presents a discussion of the following major areas related to emission measurement for the pollutants subject to the de minimis guidelines:

- Sampling and analysis methodology
- Accuracy and precision of sampling and analysis methodology
- Means of assessing the adequacy of emissions data for use in calculating emission factors.
- Implications of the variability of actual emission factors for calculating source emissions.

A search of the CCEA data base for information on the emissions of these pollutants from SCCP produced the following results:

- For Mercury, Beryllium and Fluorides: a relatively large amount of valid data.
- For Sulfuric Acid Mist (SO_3): limited data.
- For Asbestos, Hydrogen Sulfide, Methyl Mercaptan, Dimethyl Sulfide, Dimethyl Disulfide, Carbon Disulfide and Carbonyl Sulfide: no data.

The discussion in this section will therefore be limited to Mercury, Beryllium, Fluorides, and Sulfuric Acid Mist (SO_3).

It was beyond the scope of this effort to review all pertinent literature on sampling and analysis for these four pollutants. Thus, this section will briefly describe general, widely used sampling and analysis methodologies and will then present in more detail several examples from the CCEA information base.

6.1 SAMPLING METHODOLOGY

There are a limited number of widely used methods for sampling stacks for particulates and volatiles. Work prior to 1971 was typically performed with an ASTM specified train (ASTM, 1971). Since then, stack sampling typically has been performed in accordance with EPA's method 5 specifications (EPA-76). A stack sampling train now in wide use is the Source Assessment Sampling System (SASS) train, which is required by EPA-IERL on its emissions assessment programs (77.). The impinger contents of the ASTM and Method 5 trains were modified by workers who needed to trap volatile inorganic species. The SASS train impingers were designed to trap volatile inorganics. A typical sulfur species sampling train is the Controlled Condensation System (CCS) (78.). This train collects particulate sulfate on a heated filter; SO_3, as H_2SO_4, in a coil maintained at a temperature above the dew point of H_2SO_4; and SO_2 in a hydrogen peroxide filled impinger. Some chlorine and fluorine is trapped in the peroxide impinger, and the reminder is trapped in a second, sodium carbonate filled impinger.

Recent reports from the Emissions Assessment of Conventional Combustion Systems (EACCS) (1,57.) program have been used in the development of emission factors discussed in Sections 4.0 and 5.0 of this report. A major task of the EACCS program is to evaluate the existing data base. This evaluation cited eleven sources of emissions data as being particularly useful. Three of these reports will be used as examples of sampling methodology.

Bolton, et al. (5.) used a standard ASTM train to sample particulate emissions from the stack and across the electrostatic precipitator of a coal-fired utility plant. Samples were taken isokinetically across the ducts and stack diameters. Samples of coal, slag, and other process streams were taken by conventional methods (e.g., grade sampling) and composited over the test period. They also reported on laboratory tests of an impinger system for trapping volatile mercury compounds.

Curtis (8.) summarized a number of trace element emission studies performed by Ontario Hydro. Conventional methods were used to sample liquid and solid process streams. Use of a special stack sampling unit for collecting vapor phase trace elements was mentioned, but no details were given. The stacks were traversed, and sampling was isokinetic.

Schwitzgebel, et al. (4.) used conventional methods of sampling liquid and solid process streams. They used a wet electrostatic precipitator (WEP) to sample particulates in the stack. The WEP was backed up by a standard Method 5 filter to verify the collection efficiency of the WEP. Mercury was sampled by a gold amalgamation technioue. Sulfur species were trapped in hydrogen peroxide. Sampling was isokinetic at the required number of traverse points across the stack diameter.

Shih, et al, (57.) reported the use of the CCS train for sampling sulfur species at oil-fired internal combustion sources in the utility and industrial use sectors. Sampling with this train on the EACCS program is performed isokinetically at the point of average velocity.

6.2 ANALYTICAL METHODOLOGY

Analytical methods applied to trace pollutant emissions measurements are also limited. Neutron activation analysis (NAA) is a multi-element technique capable of ultratrace levels with high accuracy and precision. Spark source mass spectrometry (SSMS) is another widely used multi-element method. For most elements, SSMS has an accuracy and precision of ± 50 percent. Atomic absorption spectroscopy (AAS), both flame and flameless, is a single element technique capable of high accuracy and precision at trace and ultratrace levels. Titrimetry is commonly used for sulfur species sampled by the Goksoyr-Ross or CCS trains. Selective ion electrodes (SIE) are generally used for halogens. Selective ion electrodes are capable of accuracy and precision of about five percent.

Analytical methods generally are not the limiting factor in trace element analysis. The nature of the sample, sample handling, and particularly sample preparation can have a significant effect on the overall accuracy of a sampling and analysis program. For example, to get reasonable closure on a materials balance, solid samples (e.g., fly ash) have to be totally dissolved in order to free trace elements bound in the solid matrix for analysis. The usual method for totally dissolving inorganic solids is with a mixture of strong acids. Coal samples are usually burned in an oxygen filled calorimeter (e.g., Parr oxygen bomb) before trace element analysis.

Bolton, et al, (5.) determined mercury by flameless AA, and beryllium by NAA. Fluoride and SO_3 were not determined. They reported that NAA was good to five percent for most elements.

Curtis (8.) reported that Hg and F were determined by NAA, F by selective ion electrode, and Be by flameless AA. Table 6-1 presents the accuracies given by Curtis.

TABLE 6-1. ACCURACIES OF TRACE ELEMENT DETERMINATIONS FROM CURTIS (7)

Element	Coal	Bottom Ash	ESP Ash	Post-ESP	Ash Particulate
Be	±10%	±15%	±15%	±35%	NA
Hg	±15%	±15%	±15%	±85%	±15%
F	± 5%	±15%	±35%	±55%	±40%

TABLE 6-2. ACCURACIES OF TRACE ELEMENT DETERMINATIONS FROM SCHWITZGEBEL (1975)

Element	Coal & Coal Ash	Lime	Aqueous Samples	WEP Liquor
Be	±12%	±12%	±10%	±10%
Hg	±10%	±10%	±10%	±20%
F	± 8%	± 8%	± 8%	± 8%

Schwitzgebel et al, (4.) used AA for Hg and Be and a selective ion electrode for F. Table 6-2 presents analytical accuracies reported by Schwitzgebel.

Samples from the CCS train are the filter (particulate sulfates), the coil rinse (SO_3 as H_2SO_4), the peroxide impinger (SO_2 as H_2SO_4, Cl, and F), and the carbonate impinger (Cl and F). Fluoride is determined by selective ion electrode. The filter is extracted to remove sulfates. The filter extract and impinger contents are determined by turbidimetry. The accuracy of the analyses is ten percent.

6.3 ADEQUACY OF DATA FOR EMISSION FACTOR DEVELOPMENT

One major task of the EACCS program is the identification of gaps and inadequacies in the emissions data base for stationary conventional combustion processes (SCCP). Assessment of the adequacy of emissions data is performed by considering both the reliability and the variability of the data. The general approach to this assessment is a three step one, which is fully described in the literature (1.) and which is summarized below.

In Step 1, emissions data are screened for adequate definition of process, equipment, and fuel parameters. Also, sampling and analysis methods are assessed. If process definition is not adequate or if sampling and analysis methods are not capable of accuracy in the range ± factor of three, the data were rejected. This step eliminates data which would be of little or no use.

Step 2 consists of further engineering and statistical analysis of the emissions data to determine their internal consistency and variability. Emission factors calculated from each pollutant-unit operation pair are evaluated for consistency by comparison with emission factors from similar sites. Emission factors lying outside upper and lower bounds are discarded. The Method of Dixon, a statistical technique applicable to the rejection of single outlying points in a small group of points, is used as the rejection criterion.

The variability of emission factors is calculated from

$$V = \frac{ts(\bar{x})}{\bar{x}}$$

where $\bar{x}$ is the mean value of the emission factor, $s(\bar{x})$ is the estimated standard deviation of the mean, and t is the Student "t", the value of which depends on the degrees of freedom of the mean and the confidence level desired for the interval containing the true population mean. For the EACCS program, values of t are chosen such that the confidence interval is 95 percent.

Step 3 of the data evaluation process involves a quantitative treatment of the variability of the emission factors to assess their adequacy. This assessment is based on both the potential environmental risks associated with the emission of each pollutant and the quality of the existing emissions data.

6.4 IMPLICATIONS OF EMISSION FACTOR VARIABILITIES FOR EMISSION CALCULATIONS

Emissions from a particular combustion source are generally calculated in the following manner:

$$\text{Emissions} = (EF)\ (F)\ (H)$$

where EF is the emission factor, F is the fuel use rate of the source, and H is the heating value of the fuel. The expected uncertainty of the emission value calculated in this manner depends on the variabilities of all of the terms in the equation.

In the EACCS program, TRW calculated variabilities for the emission factors for trace elements and SO_3 for many combustion source categories. In Table 6-3 these variabilities have been grouped by fuel type. Actual variabilities greater than 70 percent are not shown, since, in many cases, they vary widely among the specific source categories, and since such a high variability would argue against the use of the emission factor at all. The 70 percent criterion used in the table is arbitrary; however, the same variability criterion is used in the EACCS study to measure the adequacy of the data base for emission factor development.

Table 6-3 indicates that the variabilities for the beryllium emission factors are consistently greater than 70 percent for all categories of coal and oil-burning boilers. In fact, the actual variabilities are often several hundred percent for beryllium emissions from coal combustion (1.). One must conclude from this that the actual emissions of beryllium from a given coal-burning source bear little relationship to calculated emission value for the pertinent source category, based on the existing emission data (i.e., using one of the factors given in Section 4.1 of this report).

Emission factors for mercury, on the other hand, have variabilities less than 70 percent for coal and oil combustion, although the variability for the mercury emission factor for gas combustion is greater than 70 percent (143 percent (1.)). The emission factor variability for fluorides from coal combustion is less than 70 percent and for fluorides from oil combustion is greater than 70 percent (96 percent (1.)). Variabilities for SO_3 emission factors are less than 70 percent for both coal and oil combustion.

TABLE 6-3. VARIABILITIES OF CALCULATED EMISSION FACTORS

Fuel	Variabilities			
	Mercury	Beryllium	Fluorides	SO_3
Coal	35%-40%	>>70%	35%-40%	19%
Oil	50%	>70%	>70%	33%
Gas	>70%	NE[a]	NE[a]	NE[a]

[a] Negligible emissions.

Source: Shih, et al, 1979 (1.).

It should be noted that variability does not necessarily represent the accuracy of sampling and analysis methods used. It more often represents variation in the parameters used to develop the emission factors:

- Concentration of element in fuel.
- High heating value of fuel.

For trace elements only:

- Fraction of ash as fly ash
- Collection efficiency of control device
- Enrichment factor for the trace element

(See equation in Section 5.1.1). Most emission factors shown in Section 4 of this report require substitution of the concentration of the element in the fuel for C in the case of trace elements and for S in the case of sulfuric acid mist. The variability of this concentration appears to be relatively low (1.), however, and, therefore, is probably not an important influence on the high variability of the beryllium emission factors. Instead, it is more likely the variability of the enrichment ratio which causes high variability in the beryllium emission factors. (Enrichment does not occur during emission of mercury, fluorides, and sulfuric acid mist). Although enrichment ratios depend on the efficiency of the control device and the consequent particle size distribution, the relationship between enrichment ratio and these and other influence parameters is not known.

The expected uncertainty of a calculated emission value depends also on the variabilities of the remaining two terms in the equation quoted earlier in this section: the fuel use rate and the heating value of the fuel. If it is assumed that the variabilities of these terms are very small compared to the variability of the emission factor, the following recommendations can be made, based on the observations in this discussion:

- Little confidence can be placed in calculated emission of beryllium from any combustion source until more sampling data are taken and better beryllium emission factors are developed.

- Calculated emissions of mercury from gas combustion and fluorides from oil combustion are somewhat uncertain until better emission factors can be developed.

- Calculated emissions of mercury, fluorides, and SO_3 from source categories not mentioned in the preceding statement are within the range of uncertainty usually anticipated for this type of calculation.

APPENDIX A: PERSONS CONTACTED FOR INFORMATION ON TOTAL REDUCED SULFUR AND REDUCED SULFUR EMISSIONS

Name	Affiliation
David Anderson	TRW
Steve Cherry	KVB Inc.
Dr. Delbert Eatough	Brigham Young University
Dr. Ed Eimutis	Monsanto Research Corporation
Dr. Warren Hamersma	TRW
William Henry	Battelle
Jim Homolya	EPA/RTP
Dr. Ralph Perhac	Electric Power Research Institute
Jake Sommers	EPA/RTP
Jim Sutherland	EPA/RTP

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16. ABSTRACT

Report presents a literature survey of the health and ecological effects associated with various air quality levels of noncriteria pollutants that are regulated under the Clean Air Act. These noncriteria pollutants include mercury, beryllium, asbestos, sulfuric acid mist, vinyl chloride, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, carbon disulfide and carbony sulfide. Nationwide emissions are estimated for each noncriteria pollutant with particular emphasis on contributions from fossil fuel combustion at stationary sources. Factors for quantifying emissions from fossil fuel combustion processes are discussed for each noncriteria pollutant.

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